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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1909.

ISSUED BY THE CHEMICAL SOCIETY.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>A.</i>	Abstracts in Journal of the Chemical Society.*
<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Phys.</i>	Annales de Chimie et de Physique.
<i>Ann. Inst. Pasteur</i>	Annales de l'Institut Pasteur.
<i>Ann. of Botany</i>	Annals of Botany.
<i>Ann. Physik</i>	Annalen der Physik.
<i>Ann. Report</i>	Annual Reports of the Chemical Society.
<i>Ann. sci. Univ. Jassy.</i>	Annales scientifiques de l'Université de Jassy.
<i>Arb. Kais. Gesund. Amt.</i>	Arbeiten der Kaiserliche Gesundheitsamt.
<i>Arch. expt. Path. Pharm.</i>	Archiv. für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Atti R. Accad. Sci. Torino.</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bio-Chem. J.</i>	The Bio-Chemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Boll. chim. farm.</i>	Bollettino chimico farmaceutico.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i>	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. Sci., St. Péters- bourg</i>	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
<i>Bull. Assoc. Chim. Sucr. Dist.</i>	Bulletin de l'Association des chimistes de Sucrierie et de Distillerie.
<i>Bull. Imp. Inst.</i>	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Centr. Bakt. Par.</i>	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Min.</i>	Centralblatt für Mineralogie, Geologie und Palaeonto- logie.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Chem. News</i>	Chemical News.
<i>Chem. Weekblad</i>	Chemische Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.

* The year is not inserted in references to 1909,

viii TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Deut. landw. Presse</i> . . .	Deutsche landwirthschaftliche Presse.
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Gummi-Zeit.</i>	Gummi-Zeitung.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Jahrb. Min. Beil.-Bd.</i> . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
<i>Jahrb. Radioaktiv. Elektro- nik</i>	Jahrbuch der Radioaktivität und Elektronik.
<i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i>	Journal of Biological Chemistry, New York.
<i>J. Chim. phys.</i>	Journal de Chimie physique.
<i>J. Gasbeleucht.</i>	Journal für Gasbeleuchtung.
<i>J. Inst. Brewing.</i>	Journal of the Institute of Brewing.
<i>J. Iron and Steel Inst.</i> . .	Journal of the Iron and Steel Institute.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers</i>	Journal of the Society of Dyers and Colourists.
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher.
<i>Landw. Versuchs-Stat.</i> . .	Die landwirtschaftlichen Versuchs-Stationen.
<i>Mem. Coll. Sci. Eng. Kyōtō</i> .	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Metallurgie</i>	Metallurgie.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. Sci.</i>	Moniteur scientifique.
<i>Oesterr. Zeitsch. Berg. Hüt- tenwesen</i>	Oesterreichische Zeitschrift für Berg- und Hüttenwesen.
<i>Pflüger's Archiv</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Zeit.</i>	Pharmazeutische Zeitung.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentrallhalle.
<i>Philippine J. Sci.</i>	Philippine Journal of Science.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift.
<i>Proc.</i>	Proceedings of the Chemical Society.
<i>Proc. Amer. Acad.</i>	Proceedings of the American Academy.
<i>Proc. Amer. Physiol. Soc.</i> .	Proceedings of the American Physiological Society.
<i>Proc. Camb. Phil. Soc.</i> . .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Physiol. Soc.</i>	Proceedings of the Physiological Society.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Quart. J. exp. Physiol.</i> . .	Quarterly Journal of experimental Physiology.
<i>Quart. J. Geol. Soc.</i>	Quarterly Journal of the Geological Society.

ABBREVIATED TITLE.	JOURNAL.
<i>Rec. trav. chim.</i> . . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. Fis. Mat. Napoli</i> . . .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
<i>Rev. gén. Chim. pure et appl.</i>	Revue générale de Chimie pure et appliquée.
<i>Sci. Proc. Roy. Dubl. Soc.</i> .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Techn. Quart.</i> . . .	Technology Quarterly.
<i>Trans.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i> . .	Transactions of the Faraday Society.
<i>Tsch. Min. Mitt.</i> . . .	Tschermak's Mineralogische Mittheilungen.
<i>Verb. Ges. deut. Naturforsch. Aerzte</i> . . .	Verhandlung der Gesellschaft deutschen Naturforscher und Aerzte.
<i>Zeitsch. anal. Chem.</i> . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem. Ind. Kolloide.</i>	Zeitschrift für Chemie und Industrie der Kolloide.
<i>Zeitsch. Elektrochem.</i> . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i> .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i> . .	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal. Chem.</i> .	Zeitschrift für physikalische Chemie Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. prakt. Geol.</i> . .	Zeitschrift für praktische Geologie.
<i>Zeitsch. Schiess. Sprengstoffw.</i> . . .	Zeitschrift für das Schiess- und Sprengstoffwesen.
<i>Zeitsch. Ver. deut. Zuckerind.</i>	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zentr. Physiol.</i> . . .	Zentralblatt für Physiologie.

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GENERAL AND PHYSICAL CHEMISTRY.

In writing the following report the policy has been adopted of dealing somewhat fully with a limited number of topics; several subjects, in which important work is in progress, have been deliberately held over for fuller treatment in a subsequent report.

Effects of Pressure.

Several series of investigations dealing with the effects of pressure have appeared during recent months. On the chemical side interesting results have been obtained by W. N. Ipatieff and his colleagues,¹ who found, for instance, that under a pressure of 100 to 125 atmospheres of hydrogen both anthracene and phenanthrene were reduced, when heated in presence of nickel oxide, to compounds such as $C_{14}H_{12}$, $C_{14}H_{14}$, $C_{14}H_{20}$, and $C_{14}H_{24}$. The experience gained in these and other similar experiments led to a solution of the long-standing problem of the precipitation of metals from solutions of their salts by hydrogen under pressure,² negative results having been obtained previously by Tammann and Nernst.³ A critical temperature was found for the precipitation of each metal; thus silver and mercury were precipitated at atmospheric temperatures under a pressure of 200 atmospheres from decinormal solutions, but copper and the more electropositive metals could not be precipitated even when the pressure was increased to 500 atmospheres. At 120—130°, however, branched crystals of pure copper were precipitated at a pressure of 100 atmospheres, cuprous oxide being formed at lower temperatures. Cobalt was precipitated at 180—200°, nickel at 200°, lead and bismuth at

¹ *Ber.*, 1908, **41**, 966; *A.*, 1908, i, 330.

² W. N. Ipatieff and W. Werchowsky, *ibid.*, 1909, **42**, 2078; *A.*, ii, 564.

³ *Zeitsch. physikal. Chem.*, 1892, **9**, 1; *A.*, 1892, 561.

240—250°. Iron was precipitated in small quantities at 400° and 420 atmospheres pressure, complete reduction being prevented by the bursting of the steel tubes; ferric oxide was, however, precipitated quantitatively from an acetate solution at 350° and 230 atmospheres. The bearing of the experiments on Nernst's theory of "electrolytic solution-tension" is discussed, the main conclusion being that this quantity must be regarded as a variable, depending on temperature and concentration, and not as a constant.

T. W. Richards and his colleagues have studied the effect of pressure on the atomic volumes of the elements,⁴ and on the specific volumes of the chlorides, bromides, and iodides of sodium, potassium, silver, and thallium.⁵ The compressibilities of the elements and their atomic volumes are often parallel properties, but this parallelism is restricted to groups of similar elements, such as the alkali metals and the series Mg, Ca, Zn, Cd, Hg; parallelism between compressibility and coefficient of expansion is most marked in the case of elements having nearly equal atomic volumes. The compressibility of the twelve salts examined increases from Cl to I, and less regularly from Ag to Na, Tl, and K. The relationship between their compressibilities and other physical properties is discussed from the point of view of Richards' hypothesis of compressible atoms. G. Jones⁶ has also applied this hypothesis to the negative coefficient of expansion of silver iodide, which he attributes to the fact that the affinity between silver and iodine increases with rising temperature. The work of Berkeley and Hartley on the compressibilities of solutions is referred to in connexion with their work on osmotic pressure (see p. 6).

The recent experiments of R. Threlfall⁷ on the allotropic change of carbon, which showed no conversion of graphite into diamond under pressures of the order of 10,000 atmospheres and at temperatures up to the melting point of magnesia, have formed the basis of a lecture,⁸ which includes a review of earlier experiments and a useful summary of the work of Tammann on sulphur, phenol, and ice. This work has been extended⁹ by the isolation of the dense modification of ice ("Ice III") which is formed at low temperatures and high pressures, and had hitherto been recognised only from the readings of a pressure gauge. In order to prepare

⁴ T. W. Richards, W. N. Stull, F. N. Brink, and F. Bonnet, *Carnegie Inst. Publ.*, 1907, No. 76; *Zeitsch. physikal. Chem.*, 1907, **61**, 77, 100; *J. Amer. Chem. Soc.*, 1909, **31**, 154; *A.*, 1907, ii, 858.

⁵ T. W. Richards and G. Jones, *J. Amer. Chem. Soc.*, 1909, **31**, 158; *A.*, ii, 214.

⁶ *J. Amer. Chem. Soc.*, 1909, **31**, 191; *A.*, ii, 210.

⁷ *Trans.*, 1908, **93**, 1333.

⁸ Royal Institution, March 19, 1909: *Nature*, 1909, **82**, 82.

⁹ G. Tammann, *Zeitsch. anorg. Chem.*, 1909, **63**, 285; *A.*, ii, 878.

it, water was compressed to 3000 kilograms per square cm., so as to prevent the formation of ordinary ice ("Ice I"), frozen to "Ice III" by cooling to -80° , and then cooled to -190° by means of liquid air. On removing the pressure, "Ice III" becomes metastable, but can be kept in this form sufficiently long to take it out of the pressure vessel and examine it. It is clear and colourless in appearance, and differs from ordinary ice in that it sinks in liquid air instead of floating. The reversion to ordinary ice takes place (when the pressure is less than 100 kg. per sq. cm.) at temperatures from -120° upwards; the mass becomes opaque and porcelain-like, or if transformed rapidly by removing from the liquid air, falls into a bulky powder melting at 0° . The cases of water and of sulphur are analogous in the existence of a triple point at which three modifications (water, "Ice I," "Ice III"; liquid, monosymmetric, orthorhombic) are stable; in the case of carbon, it is probable that diamond is throughout metastable, and can only be produced (perhaps by crystallisation from a solvent) when the temperature is low enough to reduce to zero the velocity of transformation into graphite.

An investigation closely related to the above is that of F. Montan¹⁰ on the effect of pressure on the electrical resistance of selenium. In contrast to the behaviour of manganin, the resistance of which changes only to the extent of 0.2 per cent. per 1000 atmospheres, that of selenium is reduced to the extent of 60 per cent., and at 3000 atmospheres falls to 6 per cent. of the original value; on releasing the pressure, the resistance persists at 0.2 to 0.5 of the normal magnitude, and only slowly recovers. These changes are attributed to the existence of allotropes similar to those of sulphur, but no evidence is given of any abrupt transformation comparable with those observed by Tammann in the case of sulphur and of ice.

Analogous experiments on the effect of pressure on the conductivity of electrolytes have been carried out by F. Körber¹¹ on lines laid down some years ago by A. Bogojawlensky and G. Tammann.¹² As a rule, the resistance decreases on compression, but in many cases a minimum is reached, and further compression causes an increase. This is seen in the case of solutions of potassium chloride at all temperatures from 0° to 100° ; at 0° the minimum amounts to 0.872 of the original value, and is just reached within the limiting pressure of 3000 kg. per sq. cm.; at 100° the lowest resistance, at 900 kg. per sq. cm., is 0.998 of the

¹⁰ *Ark. för. Mat. Astron. och Fysik*, 1908, 4, 1.

¹¹ *Zeitsch. physikal. Chem.*, 1909, 67, 212; *A.*, ii, 719.

¹² *Ibid.*, 1898, 27, 457; *A.*, 1899, ii, 137.

original, the ratio rising to 1.014 at 3000 kg. per sq. cm. Amongst the halogen compounds, the largest decreases of resistance are found in the case of hydrogen chloride (17 per cent. for $v=100$, $p=3000$, $t=19^\circ$) and lithium chloride (14 per cent.), then follow potassium chloride, sodium chloride, potassium bromide, sodium bromide, potassium iodide, and sodium iodide (9, 8, 6, 5, 2, and 1 per cent. respectively), the order of increasing atomic weights being broken in the case of sodium and potassium; minima of resistance at intermediate pressures appear, and become more and more pronounced, in the curves for the last six salts; for their dilute solutions the effects are additive. The curves give the impression that (as in the case of gaseous compressibilities) two opposite factors are at work, one of these producing a decrease, and the other an increase, of electrical resistance on compression; the tendency to decrease is most pronounced in solutions of hydrogen chloride at low temperatures, low concentrations, and low pressures, the tendency to increase in concentrated solutions of sodium iodide at high concentrations, high temperatures, and high pressures. The nature of these factors is not clear, but the general conclusion—that the molecular condition of the water and the degree of hydration of the ions are of great weight—is almost incontrovertible, especially in view of the parallelism which exists between the conditions which favour a decrease or increase of resistance on compression, and those which cause the development or destruction of “ice-molecules” in the solvent.

The “Piezochemical Studies” of E. Cohen and L. R. Sinnige appear to be directed mainly to the solution of the electrochemical problem of the influence of pressure on the Clark and Weston standard cells. The simplest investigation, that of the influence of pressure on solubility,^{13 14} led to opposite results in the case of cadmium and zinc sulphates, $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. In the former case, the solubility (in grams of anhydrous salt per 100 grams of water at 25°) increased from 76.80 at 1 atmosphere to 78.00 at 500 atmospheres and 78.72 at 1000 atmospheres; in the latter case, the solubility decreased from 57.95 to 57.91 and 57.55.¹⁵ Actual measurements of the voltage of cells under pressure showed in the case of the concentration cell $\text{Cd} | \text{CdSO}_4 aq. | \text{Cd-Hg}$ (12.5 per cent.), a constant pressure-coefficient, $dE/dp = 0.0000196$ volt, from 1 to 1000 atmospheres.¹⁶ In the case of the

¹³ A full account, with diagrams of the apparatus used, is given in *Trans. Faraday Soc.*, 1909, **5**, part 3.

¹⁴ *Zeitsch. physikal. Chem.*, 1909, **67**, 432, **69**, 102; *A.*, ii, 796 and 981.

¹⁵ For the influence of pressure on the miscibility of liquids, see J. Timmermans and P. Kohnstamm (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 234; *A.*, ii, 981).

¹⁶ *Zeitsch. Elektrochem.*, 1909 **15**, 76; *A.*, ii, 291.

Clark cell, the pressure-coefficient was found to be 0.0000130 volt per atmosphere, and in the case of the Weston cell, 0.00000632 at 25°. ¹⁷ These coefficients were also deduced from the work done by the pressure, owing to the change in volume of 1 gram-equivalent of the cell materials during the passage of 96,540 coulombs. The values thus deduced (0.0000130 and 0.00000697) showed a satisfactory agreement with those determined experimentally.

Analogous experiments on the influence of pressure on the thermo-electromotive force of metals have been carried out by E. Wagner, ¹⁸ who finds that in almost every case the compressed metal is shifted in the direction of antimony in the thermo-electric series.

In view of the interest taken in high-pressure work, attention may be directed to two pressure gauges described by P. W. Bridgman. ¹⁹ One of these is a direct-pressure gauge, working by means of a weighted piston; it is sensitive to 1/20,000 of the load at 1000 kg. per sq. cm., and to 1/3500 of the load at 7000 kg. per sq. cm., and is probably accurate to 0.1 per cent. As a secondary standard, a mercury resistance gauge is described, which is equally sensitive, and gives readings correct to 0.1 per cent. from 0° to 50°.

Osmotic Pressure.

Following upon the descriptions recently given of improvements in the manometers and cells ²⁰ used in the measurement of osmotic pressure, H. N. Morse and W. W. Holland ²¹ have recently described the improved methods which they have adopted for the regulation of temperature in these experiments. An exact control of this factor is of the utmost importance, both in the initial stages of the experiment when the cell is being filled and closed, and in the later stages when the final equilibrium pressure is being determined. As the volume of the cell, after closing, is practically constant, it is obvious that the use of a cold solution for filling would be followed by a thermal expansion which could only take place by driving water from the cell and thus producing a permanent increase in the concentration; in a similar manner, a warm solution would become permanently diluted if allowed to cool after the cell had been closed. In the later stages, transient changes of temperature would cause a rise or fall of the mercury in the

¹⁷ *Zeitsch. physikal. Chem.*, 1909, **67**, 513; *A.*, ii, 857.

¹⁸ *Ann. Physik*, 1908, [iv], **27**, 955.

¹⁹ *Proc. Amer. Acad.*, 1909, **44**, 201.

²⁰ *Amer. Chem. J.*, 1908, **40**, 266, 325; *A.*, 1908, ii, 1019, 1020.

²¹ *Ibid.*, 1909, **41**, 92; *A.*, ii, 299.

manometer, indistinguishable from true osmotic effects, and would also produce changes in the concentration of the solution, which would persist long after the temperature had become readjusted. With the apparatus now described, the variations in the temperature of the bath were reduced to 0.01° , whilst the temperature of the air above it differed on the average by only 0.12° . For details of the electrical heater and regulator, the original paper should be consulted.

The table published in last year's Report (p. 14) has been extended by redeterminations of the osmotic pressure of sucrose solutions at 25° and at 20° .²² In the last series, the dilution error was finally reduced to zero, and the equilibrium pressures are regarded as being correct to the second place of decimals. Unfortunately, the supply of "rock candy" sugar used in the measurements at 10° , 15° , and 25° became exhausted before the series at 20° had been completed, and it was not possible to procure a sample of equal purity; the minor purity of the loaf-sugar used for the measurements at 20° was probably responsible for the slightly greater ratio of observed osmotic pressure to calculated gas pressure found for this temperature. The mean ratios corrected by the later observations are now as follows:

Series	III.	IV.	V.	VI.	VIII.	VII.
Temperature	0°	$4-5^{\circ}$	10°	15°	20°	25°
Mean ratio O.P./gas-pressure...	[1.074]	[1.065]	1.061	1.064	1.069	1.064
Mean loss of rotation per cent.	1.73	1.45	0.22	0.10	0.00	0.20

Experiments are in progress at 30° , and a repetition of the measurements at 0° and 5° is promised; the values provisionally given for 0° and 5° are uncorrected for dilution, as this has been found to occur almost entirely after the osmotic cell has been opened. At each temperature the ratio of osmotic to gas pressure passes through a minimum value when the concentration is raised from decinormal to normal, but as some of the figures are only provisional, the table which shows this is not reproduced in the present Report.

In view of the fact that nearly the whole of the accurate work on osmotic pressure has hitherto been carried out with aqueous sugar solutions, special interest attaches to the work of the Earl of Berkeley and his colleagues on the osmotic pressures of concentrated and of dilute aqueous solutions of calcium ferrocyanide. In the case of the concentrated solutions,²³ measurements were made at 0° of (1) the density, (2) the compressibility, (3) the

²² *Amer. Chem. J.*, 1909, **41**, 1, 257; *A.*, ii, 216, 386.

²³ The Earl of Berkeley, E. G. J. Hartley, and C. V. Burton, *Phil. Trans.*, 1908, *A.*, **209**, 177; *A.*, ii, 126; *Ann. Report*, 1908, 16.

vapour pressure, and (4) the osmotic pressure at concentrations ranging from 30 to 50 grams of anhydrous salt per 100 grams of water, the observed equilibrium pressures being compared with values deduced from the three preceding quantities by means of a modified form of Porter's equation. The extraordinary accuracy attained in these experiments, as well as the accuracy of the thermodynamic reasoning, is shown by the fact that whilst the average error amounted to only 0·3 per cent., the sum of the five calculated pressures was 442·87 atmospheres, as against a total of 442·65 atmospheres for the five observed osmotic pressures, the total discrepancy amounting to only 0·05 per cent. In the case of the weaker solutions²⁴ of calcium ferrocyanide, giving osmotic pressures from 25 atmospheres downwards, the comparison was made with values calculated on a hypothetical basis from the gas equation:

Calcium Ferrocyanide.

Concentration.		Osmotic pressure.	
Grams per 100 grams of water.	Gram-mols. per litre of solution.	Observed.	Calculated (Boyle's law).
21·813	0·7175	20·33	16·08
17·610	0·5853	14·65	13·11
12·213	0·4110	9·20	9·21
7·072	0·2406	5·34	5·39

The remarkable agreement between the observed and calculated pressures at the two lowest concentrations could, in the case of an electrolyte, only be accidental. This was proved by two further series of measurements with potassium and with strontium ferrocyanides, which gave pressures deviating widely and in opposite directions from the calculated values:

Potassium Ferrocyanide.

Concentration.		Osmotic pressure.	
Grams per 100 grams of water.	Gram-mols. per litre of solution.	Observed.	Calculated (Boyle's law).
13·580	0·3547	19·25	7·95
8·897	0·2362	13·52	5·29
5·631	0·1512	9·19	3·39
3·035	0·08216	5·41	1·84
1·518	0·04129	2·93	0·93

Strontium Ferrocyanide.

23·99	0·6000	12·04	13·45
17·97	0·4542	8·59	10·18
13·01	0·3320	6·18	7·44
6·180	0·1594	3·40	3·57

Evidently the ferrocyanides are polymerised as well as ionised

²⁴ The Earl of Berkeley, E. G. J. Hartley, and J. Stephenson, *Phil. Trans.*, 1909, A., 209, 319; A., ii, 554.

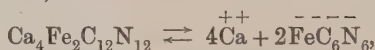
in solution, the polymerisation being predominant in the solutions of the strontium salt and the ionisation in solutions of the potassium salt, whilst in the case of the calcium salt the two factors are balanced so as to retain a normal average molecular weight.

That this polymerisation is somewhat unusual was shown by the following observations, all of which gave osmotic pressures greater than those calculated from the gas laws:

Substance.	Osmotic (obs.).	Pressure (calc.)
Magnesium camphorate	6.09	4.33
Potash alum	2.13	0.682
Sodium naphthionate	10.07	6.34
Barium benzenesulphonate	13.86	5.72
Lead benzenesulphonate	12.48*	5.16
Potassium benzenesulphonate	15.81*	8.69
Barium <i>o</i> -nitrobenzoate	16.01	6.20
Calcium naphthionate	3.95	1.79
Luteocobalt chloride	6.67*	2.94
Calcium acetate	5.20	2.36
" " " " " " " " " " " "	29.46	13.26

* Preliminary experiments.

Measurements were also made of the electrical conductivity at 0° of the calcium salt at concentrations from 17.779 to 0.001204 per cent. (2.3632*N* to 0.0001660*N*), and of the strontium salt from 24.016 to 0.001678 per cent. (2.4019*N* to 0.0001746*N*). On the assumption that these salts are bimolecular and dissociate directly into six ions, thus:



the following comparison was obtained between the observed osmotic pressures and those calculated with the help of the equivalent conductivities:

Concentration.		Osmotic pressure.	
Grams per 100 grams of water.	Double gram-mols. per litre of solution.	Observed.	Calculated.
<i>Calcium Ferrocyanide.</i>			
17.610	0.2926	14.65	12.59
12.213	0.2055	9.20	9.37
7.072	0.1203	5.34	5.71

Strontium Ferrocyanide.

23.99	0.3000	12.04	12.33
17.97	0.2271	8.59	9.77
13.01	0.1660	6.18	7.37
6.180	0.0797	3.40	3.65

Using Jones and West's measurements of the electrical conductivities of the potassium salt at 0°, the following comparison

was obtained for potassium ferrocyanide on the assumption that the salt is bimolecular and dissociates directly into ten ions:

Potassium Ferrocyanide.

Grams per 100 grams of water.	Concentration. Double gram-mols. per litre of solution.		Osmotic pressure.	
			Observed.	Calculated.
13.580	0.17735		19.25	20.18
8.897	0.1181		13.52	13.57
5.631	0.0756		9.19	8.88
3.035	0.04108		5.41	5.03
1.158	0.02064		2.93	2.72

The agreement is in each case better than could have been expected in view of the large deviations which must exist, as the authors point out, in the calculation both of osmotic pressures from the gas laws and of the coefficients of ionisation from the molecular conductivities, the latter being used without any allowance for the changing fluidity of the solutions or for partial or step-by-step ionisation of the complex salts.

In addition to the work described above on osmotic equilibrium pressure, considerable progress has been made in the study of osmotic flow. L. Vegard²⁵ has made measurements of the velocity of flow of water through a membrane under hydrostatic pressures ranging from 3 to 26 atmospheres, and under the influence of (negative) osmotic pressures ranging from 12 to 86 atmospheres. In the former case a linear relationship was found, implying that the membrane possesses an approximately constant "specific resistance," for instance:

Pressure	4.33	8.19	12.2	21.0 atmospheres
Flow ...	78	155	270	420 arbitrary units.
Ratio ...	18.0	18.9	22.1	20.0

In the case of osmosis, the steady flow was at low pressures the same as that given above, but at higher pressures deviations were soon found, and the two curves connecting pressure with flow, although at first tangential, diverged widely after leaving the origin. The conclusion is drawn that the work required to draw water through a membrane is due entirely to the mechanical resistance of the membrane to the passage of the pure liquid solvent, and that the solution as such does not enter the membrane.

The Earl of Berkeley and E. G. J. Hartley,²⁶ in a paper on "dynamic" osmotic pressures, have also made a comparison of

²⁵ *Proc. Camb. Phil. Soc.*, 1909, 15, 13; *A.*, ii, 300. Compare *Ann. Report*, 1908, 15.

²⁶ *Proc. Roy. Soc.*, 1909, A, 82, 271; *A.*, ii, 553.

hydrostatic and osmotic flow. The proportionality of hydrostatic pressure and flow is shown by the following figures:

Pressure atmos.	Rate mm./sec.	Ratio of Rates.	Ratio of pressures.
20·41	0·1075	1	1
40·82	0·2203	2·05	2
61·24	0·3240	3·01	3
81·65	0·4303	4·00	4
102·06	0·5319	4·95	5
122·47	0·6378	5·93	6

the average flow per atmosphere being 0·00528 mm. per second. The initial rates of flow were also measured when an osmotic suction was produced by well-stirred sugar solutions; the hydrostatic pressures which would have been required to produce equal flows were calculated and were compared, under the name of "dynamic" osmotic pressures, with the "static" or equilibrium osmotic pressures measured by the methods previously described:

Concentration. gm.	Rate. mm./sec.	Rate/0·00528 =dynamic O.P. atmos.	Equilibrium osmotic pressure. atmos.
750	0·571	108·2	134·7
660	0·472	89·5	100·8
540	0·315	59·7	67·5
300	0·134	25·4	26·8
96·2	0·0341	6·46	6·36
45	0·0155	2·94	2·97

For all pressures up to 7 atmospheres, a good agreement was observed in two series of experiments, but beyond this there was considerable divergence. It is suggested that in the case of dilute solutions, observations of flow may provide an easier way of measuring the small osmotic pressure than the direct equilibrium method, and that accurate observations might be made at concentrations even less than the smallest—2 grams per litre, giving an osmotic pressure of 1/7 atmosphere—used in the present series.

On account of their unique character, special interest attaches to the observations of A. J. Brown²⁷ on the "Selective Permeability of the Coverings of the Seeds of *Hordeum vulgare*." The variety *coerulescens* owes its colour to a blue pigment, which, like litmus, is turned red by acids. But the pigment is contained in the interior of the seed, and is protected by a membrane which is extraordinarily resistant to the action even of strong acids, although it is soon disintegrated by alkalis. After removing as faulty all those seeds which were reddened by normal sulphuric acid in the course of forty-eight hours, it was found that 99 per cent. remained blue at the end of five days, 95 per cent. at the end of seven days,

²⁷ *Proc. Roy. Soc.*, 1909, B, 81, 82; A., ii, 386.

74 per cent. at the end of fourteen days, 25 per cent. at the end of nineteen days, and 1 per cent. at the end of twenty-four days. This resistance to the penetration of acid was also noticed in solutions containing 9, 18, and even 36 grams of sulphuric acid per 100 c.c. From all the weaker acids the seeds freely absorb water, the acid being concentrated to a very marked extent, for example, from 4.9 grams per 100 c.c. (normal) to 7.6 grams. Hydrochloric acid of normal strength, sodium hydroxide at concentrations below 0.5 per cent., and salts, such as cupric sulphate, ferrous sulphate, potassium chromate, and silver nitrate, do not penetrate the membrane, although water is freely absorbed from their solutions.

Special interest attaches to the limited number of substances which are able to enter the seed through the protecting membrane. These include (1) water, (2) iodine, (3) mercuric chloride and cyanide, but not the sulphate or nitrate, (4) cadmium iodide to some slight extent, but not the chloride or sulphate, (5) the fatty acids from formic to butyric, trichloroacetic acid, glycollic acid (slowly), and lactic acid (very slowly), (6) ammonia, (7) alcohol, aldehyde, acetone, and ethyl acetate from their aqueous solutions, but not from the anhydrous liquids. Subsequent tests, for instance, with sulphuric acid, showed that the membrane was still intact, and had not been destroyed by these solutes. It will be seen that the only "salts" which are able to penetrate the membrane are the two mercury compounds, the aqueous solutions of which are so weakly ionised as practically to be non-electrolytes, and the feebly ionised cadmium iodide. On the other hand, it is noteworthy that no marked difference exists between the behaviour of acetic acid, which is only slightly ionised, and trichloroacetic acid, which is strongly ionised. This result may be interpreted as indicating that the question of permeability or impermeability is determined wholly by the properties of the non-ionised part of the solute, the ionised part being of itself essentially incapable of penetrating the membrane. As glycerol, sugar, and tartaric acid do not pass through the membrane, it is probable that the penetration depends to some extent on the molecular weight of the solute, even if only by retarding beyond the limits of convenient experimental observation the entry of the larger molecules. The impermeability of the membrane to mineral acids and to salts (including aminoacetic acid) may perhaps be explained on these lines as depending on the complexity of the molecules which are present in their aqueous solutions.

The maximum weight of water absorbed by the seeds ranges from about 70 to 80 per cent. Similar weights are absorbed when

the water is mixed with a solute which penetrates the membrane, for instance:

Water... ..	78.2	Alcohol... ..	74.0	Acetone	72.7
Acetic acid...	73.8	Aldehyde ...	70.6	Ethyl acetate ...	73.1

all the solutes were added to a concentration of 1 gram-molecule per litre. Solute which do not penetrate the membrane reduce the weight of water absorbed; for instance, in the case of some typical organic compounds, normal solutions gave the values:

Ethylene glycol ...	52.7	Glycine ...	41.8
Glycerol	41.5	Carbamide ...	45.5

weight-normal solutions of typical salts gave the values:

KCl... ..	38.4	NaCl... ..	37.2	NH ₄ Cl... ..	37.4
KNO ₃	41.6	NaNO ₃	38.5	NH ₄ NO ₃	38.9

(water=70.0), chlorides producing a larger effect than nitrates, and potassium salts less than sodium or ammonium salts; volume-normal solutions gave the values:

CuSO ₄	41.7	Tartaric acid	42.2
H ₂ SO ₄	37.8	Sucrose	39.3

as compared with 74.3 for water. It will be seen that the proportions of water absorbed by the seeds do not vary greatly for these different solutes, but no great significance can be attached to this, as the alteration produced by doubling or halving the concentration amounts only to 6 or 8 per cent.

In discussing the two groups into which the solutes are divided, the author suggests that "some unrecognised peculiarity in the manner in which the molecules of the two classes of solutes are combined with the molecules of the solvent water may constitute the factor which orders their different behaviour with respect to the seed-coverings." This conception is developed by H. E. Armstrong²⁸ in a note which immediately follows the paper, under the title, "The Origin of Osmotic Effects. II. Differential Septa."²⁹ It is suggested that "the compounds which penetrate the membrane, whether electrolytes or non-electrolytes, are all substances which attract water presumably only to a minor extent, and which exist to some extent in solution in an unhydrated condition; those which cannot penetrate it, on the other hand, probably all form hydrates of considerable stability in solution." The view is advanced that the membrane is not merely wetted by water, but chemically combined with it, and that molecules which are hydrolated by solution in water are seized and held back by the

²⁸ *Proc. Roy. Soc.*, 1909, B, **81**, 94; *A.*, ii, 387.

²⁹ Compare *Ann. Report*, 1907, 21.

hydrolated membrane, whilst molecules which are not hydrolated by water are able to pass freely through it.

An interesting paper in reference to the mechanism of osmosis is that of S. L. Bigelow and F. E. Bartell³⁰ on the size of the pores in porcelain required to produced osmotic effects. The size of the pores was deduced from the pressure required to force air-bubbles through a wetted porcelain disk, whilst its osmotic properties were tested in a small cell by means of a normal sugar solution adjusted to a level 8 mm. higher than that of the distilled water on the other side of the disk. It was found that the maximum pore-diameter which produced distinct osmotic effects was 0.37 micron, slightly higher figures being obtained when the pores were clogged with barium sulphate or with sulphur. In order to reconcile these dimensions—which are so much larger than the largest probable diameter of the molecules—with current views of the membrane as a solvent, the author advocates the view of Lhermite (1855), that solution itself is essentially a capillary phenomenon.

Related work on osmosis through permeable membranes has been carried out by F. Weimers,³¹ who has measured the rate of diffusion in opposite directions of water, and of the alkali salts of the halogen acids.

Attention may also be directed to the reply of L. Kahlenberg³² to the recent criticisms of E. Cohen and J. W. Commelin³³; to a paper by J. König and J. Hasenbäumer³⁴ on the measurement of osmotic pressure, especially of soils, and to a paper by A. A. Jakowkin³⁵ on the osmotic pressure of complex solutions, especially of glycerol in mixtures of ethylene glycol and water; the last paper deals with vapour pressures, and contains no direct measurements.

Freezing-point Curves: Properties of Liquefied Gases.

A number of interesting freezing-point curves have been plotted, mainly in the case of liquid or gaseous mixtures which could only be frozen with the help of modern low-temperature methods. The freezing-point curve for aqueous ammonia has been investigated independently by F. F. Rupert³⁶ and by A. Smits and S. Postma,³⁷

³⁰ *J. Amer. Chem. Soc.*, 1909, **31**, 1194; *A.*, ii, 979.

³¹ *Ann. Physik*, 1908, [iv], **27**, 1081.

³² *J. Physical Chem.*, 1909, **13**, 93; *A.*, ii, 301.

³³ *Zeitsch. physikal. Chem.*, 1908, **64**, 1; *A.*, 1908, ii, 801; *Ann. Report* 1908, 17.

³⁴ *Zeitsch. angew. Chem.*, 1909, **22**, 1009; *A.*, ii, 555.

³⁵ *Zeitsch. physikal. Chem.*, 1909, **67**, 309; *A.*, ii, 796.

³⁶ *J. Amer. Chem. Soc.*, 1909, **31**, 866; *A.*, ii, 726.

³⁷ *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 186; *A.*, ii, 997.

and is remarkable in that practically identical freezing points are found for ammonia (-78°), ammonium hydroxide, $\text{NH}_3\cdot\text{H}_2\text{O}$ (-79° or -77°), and ammonium oxide, $2\text{NH}_3\cdot\text{H}_2\text{O}$ (-79° or -78°). The eutectic point for ice and ammonium hydroxide is about -113° at 33 per cent. NH_3 , but the liquid is so viscous at these temperatures that it can hardly be stirred. E. Baud and L. Gay,³⁸ who have investigated the contraction and heat liberation on mixing water and liquid ammonia, found a maximum effect for $\text{NH}_3\cdot 0.9\text{H}_2\text{O}$ and $\text{NH}_3\cdot 1.109\text{H}_2\text{O}$ respectively, indicating that ammonium hydroxide exists, not only at -79° , but also at atmospheric temperatures.

The freezing-point curve for aqueous hydrochloric acid³⁹ indicated the existence of a trihydrate, $\text{HCl}\cdot 3\text{H}_2\text{O}$, melting at -24.4° , a dihydrate, $\text{HCl}\cdot 2\text{H}_2\text{O}$, melting at -17.7° , and a monohydrate, melting at -15.35° .

After forming the monohydrate (under considerable pressure), the solvent powers of water for hydrogen chloride are practically exhausted. Any further addition of hydrogen chloride floats on the surface of the fused or solid monohydrate as a liquid layer containing something like 99.9 per cent. of hydrogen chloride, which freezes or becomes gaseous almost independently of the aqueous layer, the composition of which varies from 67 per cent. of hydrogen chloride at -15° to 62 per cent. at $+55^{\circ}$. The critical temperature of hydrogen chloride was found to be $+55^{\circ}$, and the critical density 0.43; the inability of the liquid to dissolve even small quantities of water is very remarkable.

The properties of liquid chlorine have been investigated by F. M. G. Johnson and D. McIntosh,⁴⁰ who find the freezing point to be -101.5° and the boiling point -33.7° ; the density at the latter temperature was 1.568 (mol. vol. 22.6). The only solute that showed electrolytic properties was a mixture of ether and hydrogen chloride, giving rise, perhaps, to the oxonium chloride, $\text{Et}_2\text{O}\cdot\text{HCl}$.

The existence of such compounds has been demonstrated by the observations of G. Baume⁴¹ on the freezing points of gaseous mixtures. The compounds prepared were $\text{Me}_2\text{O}\cdot\text{HCl}$, melting at -94° ; $\text{Me}_2\text{O}\cdot 4\text{HCl}$, melting at -102° ; and $\text{Me}_2\text{O}\cdot\text{SO}_2$, melting at -91.7° . The following melting points were also recorded: Hydrogen chloride, -111° ; sulphur dioxide, -72.3° ; methyl chloride, -91.5° ; methyl ether, -138.5° .

³⁸ *Compt. rend.*, 1909, **148**, 1327; *A.*, ii, 558.

³⁹ *J. Amer. Chem. Soc.*, 1909, **31**, 851; *A.*, ii, 725.

⁴⁰ *Ibid.*, 1138; *A.*, ii, 881.

⁴¹ *Compt. rend.*, 1909, **148**, 1322; *A.*, ii, 545.

Freezing-point curves have also been plotted (1) for aqueous phosphoric acid,⁴² showing maxima for H_3PO_4 , m. p. $42\cdot30^\circ$, and $\text{H}_3\text{PO}_{4\frac{1}{3}}\text{H}_2\text{O}$ (Joly's hydrate), m. p. $29\cdot35^\circ$, and a transition point from H_3PO_4 to $\text{H}_3\text{PO}_{4\frac{1}{6}}\text{H}_2\text{O}$ at $26\cdot2^\circ$; (2) for aqueous sodium sulphate up to the critical temperature of water,⁴³ when the solubility becomes practically zero, and (3) for aqueous salt solutions,⁴⁴ showing the separation of $\text{NaCl}\cdot2\text{H}_2\text{O}$ instead of anhydrous salt at all temperatures below -1° , and giving for the eutectic point $-21\cdot3^\circ$ and 30·7 per cent. NaCl .

Freezing-point Curves: Fused Salts and Alloys.

The eutectic for silver and ammonium nitrates (48·75 per cent. AgNO_3 , $102\cdot4^\circ$) has been investigated by F. M. Flawitzky,⁴⁵ whilst that for silver and thallium nitrates (equimolecular proportions, 72°) has been observed by J. Guinchant,⁴⁶ who has made use of this salt and of mercuric bromide⁴⁷ as a cryoscopic solvent.

Normal values were obtained for the molecular weight of lithium, potassium, thallium, and lead nitrates and silver fluoride, chloride, iodide, iodate, and sulphate dissolved in silver nitrate; mercurous, antimony, ammonium, potassium, silver, and thallium bromides gave readings indicating partial polymerisation when dissolved in mercuric bromide. The sudden expansion which takes place when silver nitrate passes from the monoclinic to the orthorhombic form on cooling below 159° invariably breaks the test-tube in which it is contained.

The cryoscopic behaviour of alloys of lead and tin has been investigated by W. Rosenhain and P. A. Tucker,⁴⁸ and by P. N. Degens.⁴⁹ The eutectic is at $182\cdot5^\circ$ and 37 per cent. lead (R. and T.) (24·4 atoms per cent., D.), but whereas the tin which separates does not retain more than 0·21 atom per cent. of lead (D.), the lead retains 12 atoms per cent. (D.) (16 per cent., R. and T.) of tin in solid solution.

Dissociation.

Two important limitations of the simple theory of dissociation have been pointed out during the year. H. Le Chatelier,⁵⁰ in a

⁴² *J. Amer. Chem. Soc.*, 1909, **31**, 1183; *A.*, ii, 998.

⁴³ A. Smits and J. P. Wuite, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 244; *A.*, ii, 985.

⁴⁴ C. Matignon, *Compt. rend.*, 1909, **148**, 550; *A.*, ii, 390.

⁴⁵ *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 739; *A.*, ii, 876.

⁴⁶ *Compt. rend.*, 1909, **149**, 569; *A.*, ii, 860.

⁴⁷ *Ibid.*, 479; *A.*, ii, 790. See *ibid.*, 1907, **145**, 68, 320; *A.*, 1907, ii, 667, 737.

⁴⁸ *Phil. Trans.*, 1908, A, **209**, 89; *A.*, 1908, ii, 1038.

⁴⁹ *Zeitsch. anorg. Chem.*, 1909, **63**, 207; *A.*, ii, 888.

⁵⁰ *Compt. rend.*, 1909, **149**, 250; *A.*, ii, 721.

paper on the "Law of Fixed Dissociation Pressures," calls attention to the great discrepancy which exists in the experimental figures even for the temperature at which the dissociation pressure of chalk becomes equal to one atmosphere. He suggests that the occlusion of gas by the dissociating powder is of great importance, and that this source of error might be eliminated by immersing the solid in a suitable liquid, for instance, a mixture of fused carbonates, which would be in equilibrium with the gaseous carbon dioxide on the one hand, and with the solid chalk and lime on the other. A similar source of complexity is suggested by L. Wöhler and W. Frey,⁵¹ in two papers on "Solid Solutions in the Dissociation of Cupric Oxide and the Oxides of Platinum," the suggestion being that the solid product of dissociation (for example, Cu_2O) forms a solid solution with the original material (CuO), and so alters materially its dissociation pressure. It is, however, noteworthy that H. W. Foote and E. K. Smith⁵² were able to plot satisfactory dissociation curves for copper oxide from 900° to 1050° and from 15.8 to 239 mm. pressure of oxygen without encountering any trouble from this source, and that the oxide, Co_3O_4 , also gave without difficulty a smooth curve from 800° to 970° and from 10 to 765 mm. of oxygen. It appears, therefore, that the law of constant dissociation pressures can be verified, at least in a number of cases, by actual experiment. The observed numbers were, however, not even of the same order of magnitude as those calculated by Stahl with the help of Nernst's equation.

Interesting work on gaseous dissociation has been carried out by M. Bodenstein and M. Katayama,⁵³ who have made use of a spiral silica manometer⁵⁴ of the anæroid type to study the dissociation of hydrated sulphuric acid and nitrogen peroxide, two substances which would attack the mercury of other types of pressure gauges. This instrument is particularly sensitive when surrounded by air under adjustable pressure, so that it can be used as a zero instrument; the dissociating material is then enclosed in the bulb of the silica manometer, the temperature being determined by a thermal junction enclosed in a silica tube, which is sealed into the bulb. Figures are given for the dissociation of sulphuric acid from 325° to 477° , and of nitrogen peroxide from 20° to 701° . A similar method has been used by G. Preuner and W. Schupp⁵⁵ to investigate the dissociation of hydrogen sulphide from 555° to

⁵¹ *Zeitsch. Elektrochem.*, 1909, **15**, 34, 129; *A.*, ii, 238, 322.

⁵² *J. Amer. Chem. Soc.*, 1908, **30**, 1344; *A.*, 1908, ii, 847.

⁵³ *Zeitsch. Elektrochem.*, 1909, **15**, 244; *A.*, ii, 468.

⁵⁴ Abegg, *Zeitsch. physikal. Chem.*, 1908, **61**, 455; *A.*, 1908, ii, 157; Johnson, *ibid.*, 457; *A.*, 1908, ii, 157.

⁵⁵ *Zeitsch. physikal. Chem.*, 1909, **68**, 157; *A.*, ii, 977.

1132°. In each case a satisfactory agreement was observed with values calculated from Nernst's equation.

The same authors,⁵⁶ have also studied the dissociation isotherms of sulphur from 300° to 850° with the help of the silica manometer. Their observations indicate the existence in the vapour of S₈, S₆, and S₂, whilst S₁ may appear at pressures below 30 mm. By using Nernst's equation, the proportions of the three chief forms were calculated, as well as the heat changes involved in their transformation.

Nernst's equation has also been applied with satisfactory results by A. Holt, jun.,⁵⁷ to the dissociation of water, the discrepancies previously observed⁵⁸ having been traced to errors in the measurement of temperature.

Viscosity and Fluidity.

Important progress has been made in the study of viscosity both as an independent physical property and in its relationship to other properties such as surface-tension and ionic mobility. M. Brillouin⁵⁹ has reviewed the data of Thorpe and Rodger in order to elucidate the relationship between viscosity and temperature. He concludes that Slotte's formula:

$$\eta = \frac{c}{(a + t)^n}$$

is not the most advantageous, and advocates the use of the hyperbolic formula of Graetz:

$$\eta = A \frac{t - t_0}{t - t_1}$$

In this formula, t_0 represents a temperature at which $\eta = 0$, whilst t_1 would give $\eta = \infty$, thus agreeing satisfactorily with the experimental data, which place t_0 a little above the critical temperature, and t_1 a little below the freezing point.

Graetz's formula was rejected by Thorpe and Rodger, as it could not be applied to water or to alcohols, but the author is able to show that it represents accurately the behaviour of a large range of non-polymerised liquids, and only breaks down in the case of substances which exhibit abnormally great surface-tensions at lower temperatures, and may therefore be regarded as undergoing association or polymerisation when allowed to cool (compare Eötvös

⁵⁶ *Zeitsch. physikal. Chem.*, 1909, **68**, 129.

⁵⁷ *Phil. Mag.*, 1909, [vi], **17**, 715; *A.*, ii, 468.

⁵⁸ Nernst and von Wartenberg, *Zeitsch. physikal. Chem.*, 1906, **56**, 534; *A.*, 1906, ii, 729. Langmuir, *J. Amer. Chem. Soc.*, 1906, **28**, 1357; *A.*, 1906, ii, 848. Holt, jun., *Phil. Mag.*, 1907, [vi], **13**, 630; *A.*, 1907, ii, 450.

⁵⁹ *Ann. Chim. Phys.*, 1909, [viii], **18**, 197; *A.*, ii, 367.

and Ramsay and Shields). For such compounds, a more complex formula :

$$\eta = A \sqrt{T} \frac{(t - t_1)^2 + c}{(t - t_0)^2 + c'} \quad (T = \text{absolute temperature})$$

is proposed to replace the series of formulæ used by Thorpe and Rodger to cover their observations on liquids like *tert.*-amyl alcohol.

These views of Brillouin as to the existence of a normal type of viscosity-temperature curve for simple substances derive additional interest from the fact that similar conclusions have been drawn by E. C. Bingham and Miss J. P. Harrison,⁶⁰ who have expressed this conception in a simpler form, and, with the help of many additional data, have made several important deductions from it. No less than 87 liquids were examined at temperatures ranging from 0° to 160°, and in the case of 38 a *linear relationship between fluidity and temperature* was found to exist; in addition, all other simple, and many associated, liquids gave curves which were almost linear. The slope of these curves is characteristic, and is usually constant in a given homologous series. The authors prefer to express their observations by giving as the chief constant for each liquid the (absolute) temperature at which the fluidity would reach an arbitrary fixed value, $f = 200$. These temperatures proved to be additive quantities, and the following atomic constants were deduced :

$$\begin{array}{lll} \text{H} = 59 \cdot 2^\circ & \text{C} = -95 \cdot 7^\circ & (\text{CH}_2 = +22 \cdot 7^\circ) \\ \text{Cl} = 136 \cdot 3^\circ \text{ in monochlorides to } 109 \cdot 5^\circ \text{ in tetrachlorides.} & & \\ \text{O} = 24 \cdot 2^\circ & \text{S} = 76 \cdot 5^\circ & \\ \text{Each double bond} = +114 \cdot 4^\circ. & & \end{array}$$

Using these constants, the calculated values for non-associated liquids usually fall within 1° of the temperatures deduced experimentally. In the case of associated liquids, larger values are found, and from these the association-coefficient can be deduced. This method gives for water (H_2O) 2·31, for acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) 1·77, and for alcohol ($\text{C}_2\text{H}_6\text{O}$) 1·83.

In connexion with the experimental measurement of viscosity, it may be noted that the flow of liquids is influenced in a very marked way by the pressure that is used. E. Bose and D. Rauert⁶¹ have made measurements at pressures from 0·005 to 2 kilos. per sq. cm., and find that whilst Poiseuille's law holds good for low pressures, very marked deviations are found when the pressure is increased; in some instances the relative rates of flow are reversed, the more viscous of two liquids flowing the more readily, and becoming apparently the less viscous, at high pressures.

⁶⁰ *Zeitsch. physikal. Chem.*, 1909, **66**, 1; *A.*, ii, 382.

⁶¹ *Physikal. Zeitsch.*, 1909, **10**, 406; *A.*, ii, 645.

Viscosity of Mixtures: Formation of Compounds.

The viscosity of mixtures has been largely studied in recent years with the view of elucidating the relationship between viscosity and electrolytic conductivity, but much work has also been done in the hope that the viscosity-concentration curves of binary mixtures might afford evidence of the existence of complex molecules. Most of the measurements have been made at a constant temperature, but measurements at temperatures 1° below the boiling point of the liquid have been described by A. Findlay.⁶² The results, which appear to be very similar to those obtained at constant temperature, show that in four cases ($\text{C}_6\text{H}_6, \text{CH}_4\text{O}$; $\text{C}_6\text{H}_6, \text{C}_2\text{H}_6\text{O}$; $\text{CHCl}_3, \text{C}_2\text{H}_6\text{O}$; $\text{CCl}_4, \text{C}_2\text{H}_6\text{O}$) the viscosity was less than that calculated from the mixture law; in two cases ($\text{C}_6\text{H}_6, \text{CCl}_4$; $\text{CHCl}_3, \text{COMe}_2$) the observed values were greater than the calculated. The sagging of the viscosity-concentration curves is of such frequent occurrence as to be a normal characteristic of binary mixtures, but this renders it very difficult to gauge the extent to which abnormality may be asserted when the curves are only slightly sagged or rise above the straight line of the simple mixture law. It is, therefore, remarkable that so little attention has been paid to the method advocated by Bingham, in 1906,⁶³ of plotting the reciprocal of the viscosity (that is, the fluidity) against the concentration. This method has the advantage that a linear relationship is found, not only in mixtures which give linear viscosity curves ($\text{C}_6\text{H}_6, \text{CHCl}_3$; $\text{C}_6\text{H}_6, \text{C}_6\text{H}_5\text{Me}$),⁶⁴ but also in a very large range of cases (for example, $\text{C}_6\text{H}_6, \text{C}_4\text{H}_{10}\text{O}$) in which the viscosity curves sag considerably. It appears, indeed, that the straight line is the normal type for the fluidity-concentration, as well as for the fluidity-temperature curves, and, if this be so, the readiness with which abnormalities may be recognised is enormously increased.

The idea that a pronounced maximum of viscosity may be taken as an indication of the existence of complex molecules in a mixture is a natural sequel to the observation that the viscosity and molecular weight increase together in a regular manner in homologous series, the logarithm⁶⁵ of the viscosity being related to the molecular weight by a linear law in several series of compounds.⁶⁶ In one case, at least—the monohydrate of sulphuric

⁶² *Zeitsch. physikal. Chem.*, 1909, **69**, 202; *A.*, ii, 975.

⁶³ *Amer. Chem. J.*, 1906, **35**, 195; *A.*, 1907, ii, 218.

⁶⁴ The viscosities of the constituents being nearly equal, the curves are approximately horizontal.

⁶⁵ The use of the logarithm to detect a linear relationship is equivalent to the use of the reciprocal as advocated by Bingham (see above).

⁶⁶ *Trans.*, 1907, **91**, 83.

acid, $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ —the existence and the cause of such a maximum are established beyond doubt by the observations of Knietsch,⁶⁷ of Dunstan and Wilson,⁶⁸ and of Kremann and Ehrlich.⁶⁹ Controversy has been aroused in reference to the application of the method to cases in which the existence of complexes is less certain, the chief points at issue being whether the concentration of maximum viscosity (1) is independent of the temperature, and (2) occurs at a concentration corresponding with the composition of a definite hydrate or other complex.⁷⁰ Apart from the case of the hydrate, $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$, in which the concentration of maximum viscosity is constant between 0° and 75° , the evidence in reference to the first point is conflicting. Traube found for the system $\text{CH}_4\text{O}, \text{H}_2\text{O}$ a shifting of the maximum from 32 to 40 per cent. CH_4O between 0° and 30° ; but Getman found no change between 0° and 63° ; Arrhenius and Traube observed a large shifting in the case of ethyl alcohol and water between 0° and $+55^\circ$ and 0° and 30° respectively, but this was not shown by the measurements of Dunstan and Thole⁷¹ at 20° and 30° ; for mixtures of acetic acid and water, aniline and phenol, and aniline and cresol, the concentrations of maximum viscosity are invariant over a wide range of temperature. So far as the second point is concerned, it is clear that the maximum of viscosity does not always correspond with the composition of the simplest compound, nor of the compound which separates on crystallisation, although it is conceivable that other compounds of too low melting point or too high solubility to separate on cooling may exist in the liquid and determine the form of the viscosity-concentration curves. The theory of the viscosity maximum is much less clearly established than in the case of freezing-point curves, and it is noteworthy that Findlay⁷² attaches greater importance to the point of maximum deviation from the linear law than to the points of maximum or minimum viscosity.

In addition to the cases cited above, maxima of viscosity have been described by D. E. Tsakalotos⁷³ in the case of the aqueous solutions of pyridine, piperidine, nicotine, triethylamine, and *iso*-butyric acid. The last three solutions separate into two layers on slight cooling, but mixtures of amylene and aniline, which behave

⁶⁷ *Ber.*, 1901, **34**, 4069; *A.*, 1902, ii, 134.

⁶⁸ *Trans.*, 1907, **91**, 85.

⁶⁹ *Sitzungsber. Wien. Akad.*, 1907, **116**, 749; *Monatsh.*, 1907, **28**, 831; *A.*, 1907, ii, 747.

⁷⁰ Dunstan and Thole, *Trans.*, 1909, **95**, 1556; G. Senter, *Proc.*, 1909, **25**, 292.

⁷¹ *Loc. cit.*

⁷² *Loc. cit.*

⁷³ *Bull. Soc. chim.* 1909, [iv], **5**, 397; *Compt. rend.*, 1909, **148**, 1324; *Zeitsch. physikal. Chem.*, 1909, **68**, 32; *A.*, i, 412, ii, 553, 975.

in the same way, show a minimum of viscosity, so the two properties appear to be independent.

A. Smith and A. W. C. Menzies⁷⁴ were unable to detect any break in the viscosity-concentration curves for concentrated aqueous solutions of orthophosphoric acid, which, on cooling, deposited crystals of the hydrates, $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{H}_3\text{PO}_4 \cdot \frac{1}{10}\text{H}_2\text{O}$. As the curve of specific conductivities is also smooth, it is probable that these hydrates are dissociated by fusion to such an extent as not to form the major constituents of the solutions. A smooth curve of specific conductivities was also plotted from 0 to 100 per cent. H_3PO_4 , with a maximum conductivity at 43 per cent., by H. E. W. Phillips,⁷⁵ but only three observations were made between 90 and 100 per cent., so it would scarcely have been possible to detect any irregularity within these limits.

Viscosity and Conductivity.

The close relationship which exists between the viscosity (or fluidity) of a solution and its electrical conductivity has during recent years become generally recognised. The most striking results have followed from the study of dilute solutions in which the effects produced by variations of the "coefficient of ionisation" are at a minimum, and many investigations have sought to eliminate these effects altogether by extrapolating to infinite dilution, and deducing a relationship between the fluidity of the solvent and the limiting conductivities of the solute or of its ions.⁷⁶ This was done by Kohlrausch,⁷⁷ who was thus enabled to show that the limiting conductivities of a series of acids, bases, and salts, investigated by Deguisne,⁷⁸ at temperatures from 2° to 34°, could all be reduced by extrapolation to a fictitious zero value at -38.5° , and that the fluidity of the solvent behaved in identically the same way, tending towards a zero value at the same temperature. This method was also used by Walden,⁷⁹ who, reversing the procedure of Kohlrausch, measured the conductivity of a single solute, tetraethylammonium iodide, $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, in forty different solvents, and showed that the limiting conductivity of this salt was at least approximately proportional to the fluidity of the solvent, the

⁷⁴ *J. Amer. Chem. Soc.*, 1909, **31**, 1191; *A.*, ii, 999.

⁷⁵ *Trans.*, 1909, **95**, 59.

⁷⁶ In the case of purified water—the most dilute of aqueous solutions—no extrapolation is necessary, and a direct proportionality exists between the fluidity and the actual measured conductivity (see *Proc. Roy. Soc.*, 1902, **71**, 48).

⁷⁷ *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1026; compare *ibid.*, 1902, 572; *A.*, 1902, ii, 489.

⁷⁸ *Diss.*, Strasburg, 1895.

⁷⁹ *Zeitsch. physikal. Chem.*, 1906, **55**, 207; *A.*, 1906, ii, 335.

product $\eta \times \mu_{\infty}$ having an average value 0.7. The validity of this general rule has been questioned by Dutoit and Duperthuis,⁸⁰ who, after making measurements of viscosity from 0° to 40° or 80°, found that the magnitude of the product $\eta\mu_{\infty}$ was affected by changes of temperature even when all other conditions were kept constant. Thus, for solutions of sodium iodide in pyridine, the product varied from 0.573 at 0° to 0.559 at 80°, and in *iso*amyl alcohol to an even larger extent, from 0.374 to 0.225. M. R. Schmidt and H. C. Jones⁸¹ call attention to similar discrepancies in the case of potassium iodide, which gave for $\eta\mu_{\infty}$ the values 0.72 in methyl alcohol, 1.32 in ethylene glycol, and 2.10 in glycerol. Walden's rule is thus obviously not an exact general law, but may nevertheless be of considerable value, not only as a basis for rough predictions, but as a means of recognising abnormality in different solvents; the favourable results which Walden himself obtained may have been due in part to his choice of a "normal" solute; the inert and bulky $C_8H_{20}N'$ group might be expected to form complex ions far less readily than Na' or K' , and its ionic size would therefore be much less affected by changes in the nature of the solvent.

The influence of viscosity on electrical conductivity has also been studied extensively during recent years by taking one or two typical solutes and measuring their conductivity in a *mixed* solvent, the viscosity of which can be changed gradually by altering the proportions of the ingredients of the mixture. This method has been employed by H. C. Jones and his colleagues since 1902, the solvents employed being water, the alcohols, acetone, nitrobenzene, and, most recently,⁸² glycerol. The last paper contains a twenty-page review of their previous work, to which reference may be made by those who are interested in this branch of investigation. The earlier papers on mixed solvents were reprinted by the Carnegie Institution in 1907.

Measurements of conductivity and viscosity in mixed solvents have also been made by S. W. Serkoff,⁸³ using solutions of lithium chloride, bromide, iodide, and nitrate, sodium iodide and salicylate, and ammonium thiocyanate in water, methyl alcohol, ethyl alcohol, and acetone. The behaviour of lithium nitrate and cadmium iodide in binary and ternary mixtures of these solvents has been studied by H. C. Jones and E. G. Mahin.⁸⁴

⁸⁰ *J. Chim. Phys.*, 1908, **6**, 726; *A.*, ii, 125.

⁸¹ *Amer. Chem. J.*, 1909, **42**, 95; *A.*, ii, 717.

⁸² M. R. Schmidt and H. C. Jones, *ibid.*, 1909, **42**, 37; *A.*, ii, 717.

⁸³ *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 399; 1909, **41**, 1; *A.*, ii, 372.

⁸⁴ *Amer. Chem. J.*, 1909, **41**, 433; *A.*, ii, 539; *Zeitsch. physikal. Chem.*, 1909, **69**, 389; *A.*, ii, 957.

. An extensive investigation of the conductivity and fluidity of solutions of lithium nitrate in mixtures of pyridine and water over the whole range from 0 to 100 per cent. has been made by Hartley, Thomas, and Applebey.⁸⁵ As both solvents possessed ionising properties, the conductivity-concentration (of solvent) curves were of a complex character. They were simplified somewhat by extrapolating to infinite dilution, and again by correcting for the changing viscosity of the solvent, but even then an inflected curve was obtained showing a range of variation from 109.4 to 61.0, perhaps on account of variations of ionic size, or perhaps from a lack of direct proportionality between fluidity and mobility (see below).

W. H. Green⁸⁶ has measured the conductivity and viscosity of solutions of hydrogen chloride and lithium chloride in mixtures of sucrose and water, these mixtures having the advantage that the volume changes which accompany dissolution are exceptionally small,⁸⁷ and vanish completely in the case of a 65 per cent. solution of sucrose at 25°. He concludes that the decrease of conductivity which results from the addition of sugar to an aqueous solution of hydrogen chloride is not proportional to the decrease of fluidity,⁸⁸ but that it is related to it by an expression of the type $\mu_{\infty} = k f^n$, where the best value for n is 0.55 for hydrogen chloride and 0.70 for lithium chloride; the average value is taken as $n = \frac{2}{3}$ approximately, but the actual value is influenced by the nature of the solute and of the mixed solvent.⁸⁹

This conclusion derives additional interest and importance from the fact that similar considerations apply to the relationship between the fluidity and ionic mobility of aqueous solutions when these are modified continuously by changing the temperature instead of by the addition of a foreign substance. From the experiments of A. A. Noyes and his colleagues, J. Johnston⁹⁰ has deduced for a series of ions the following coefficients:

	K.	Na.	NH ₄ .	Ag.	$\frac{1}{2}$ Ba.	$\frac{1}{2}$ Ca.	$\frac{1}{3}$ La.
n	0.887	0.97	0.891	0.949	0.986	1.008	1.03
$\log k$	+0.054	-0.281	+0.045	-0.143	-0.212	-0.286	-0.253
μ_{∞} for 0°	40.4	26	40.2	32.9	33	30	35

⁸⁵ *Trans.*, 1908, **93**, 538.

⁸⁶ *Ibid.*, 2023, 2049.

⁸⁷ Compare R. Olizy, *Bull. Assoc. Chim. Sucr. Dist.*, 1909, **27**, 60; *A.*, ii, 795.

⁸⁸ Fawsitt (*Proc. Roy. Soc. Edin.*, 1903, **25**, 51) found that carbamide produced proportional changes of conductivity and of fluidity when added in small quantities to aqueous solutions of hydrogen chloride, potassium chloride, and sodium hydroxide.

⁸⁹ It is noteworthy that the "intrinsic conductivity," u/f , of solutions of lithium chloride in water passes through a minimum value at a concentration of 8*N* (compare sodium hydroxide, *Phil. Trans.*, 1905, **A**, **204**, 318).

⁹⁰ *J. Amer. Chem. Soc.*, 1909, **31**, 1010; *A.*, ii, 854.

	Cl.	NO ₃ .	C ₂ H ₃ O ₂ .	$\frac{1}{2}$ SO ₄ .	$\frac{1}{2}$ C ₂ O ₄ .	$\frac{1}{3}$ C ₆ H ₅ O ₇ .	$\frac{1}{4}$ FeC ₆ N ₆ *
n	0.88	0.807	1.008	0.944	0.931	0.972	0.929
$\log k$	+0.074	+0.194	-0.455	-0.037	-0.043	-0.146	+0.139
μ_{∞} for 0°	41.1	40.4	20.3	41	39	36	58

It will be noticed that the more mobile of the univalent ions, K, NH₄, Cl, NO₃ (μ_{∞} greater than 40), are those which show the greatest deviation from the linear law, the index n being less than 0.9 in each case. The less mobile ions, Na, C₂H₃O₂ (μ_{∞} 26 and 20), give an index very near to unity (0.97, 1.008), the proportionality between mobility and fluidity being here almost exact. That this proportionality existed in the case of the more sluggish ions between 2° and 34° was already familiar from the work of Kohlrausch⁹¹; the work of Johnston extends the relationship between fluidity and mobility to a wider range of temperatures, and by the use of the index n affords a convenient method of expressing it in a simple general form.

Fused Salts and Complex Ions.

It is of interest to note that in the case of fused salts at temperatures up to 500°⁹² the ratio μ/f is either constant or decreases with rising temperature exactly as in the case of aqueous solutions. In the case of fused potassium dichromate, potassium nitrate, and mixtures of potassium and sodium nitrates, it remains constant over a range of more than one hundred degrees. In the case of sodium nitrate there is a decrease of 4 per cent. between 350° and 450°; silver nitrate shows a decrease of 4 per cent. between 250° and 350°, and lithium nitrate a decrease of nearly 10 per cent. between 250° and 300°; similar decreases are also observed in fused lead chloride and bromide. These decreases are attributed by the authors exclusively to a diminution in the (unknown) coefficients of ionisation, but might equally well be explained on the lines set forth above for aqueous solutions as due, at least in part, to a lack of direct proportionality between the fluidity of the liquid and the mobility of the ions.

In the case of fused sodium metaphosphate, NaPO₃,⁹³ a remarkable increase of fluidity, in the ratio 1:3, between 650° and 750° is not accompanied by any abnormal increase of conductivity; this lack of proportionality disappears, however, above 900°, and may perhaps be attributed to some fundamental change in the character of the electrolyte. This view is supported by the fact that

⁹¹ *Loc. cit.*

⁹² H. M. Goodwin and R. D. Mailey, *Physical Review*, 1907, **25**, 469; 1908, **26**, 28; H. M. Goodwin and H. T. Kalmus, *ibid.*, 1908, **27**, 322.

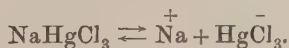
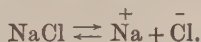
⁹³ K. Arndt, *Zeitsch. Elektrochem.*, 1907, **13**, 809; K. Arndt and A. Gessler, *ibid.*, 1908, **14**, 662, 665; *A.*, 1908, ii, 87, 923.

"solutions" of the salt in fused boric anhydride at 900° give a constant ratio of molecular conductivity to fluidity ($\mu/f=74.3, 73.8, 73.3, 73.7$) over the range from 100 to 0.5 per cent. NaPO_3 , whilst the molecular conductivity itself changes in the ratio 49.5 to 0.67. As the molecular conductivity (even after correcting for changes of fluidity) does not increase on dilution, the author adopts the view that the fused salt is completely ionised—an opinion which is in marked contrast to that of Goodwin cited above.

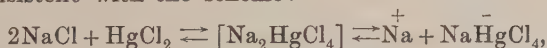
H. W. Foote and N. A. Martin⁹⁴ have made a similar series of observations on the conductivity at 282° of "solutions" in fused mercuric chloride, a salt which is itself a very poor conductor, but acquires a considerable conductivity on the addition of a small amount of an alkali chloride. Here again the remarkable observation was made that the molecular conductivity *decreased* with increasing dilution, as is clearly shown in the following table:

V (litres).	CsCl.	KCl.	NH_4Cl .	NaCl.	CuCl.
2	—	81.0	—	61.5	70.0
4	—	66.5	70.0	47.0	46.0
5	70.0	62.0	64.5	43.0	42.0
8	60.5	54.0	55.2	34.0	34.0
10	57.0	50.5	52.0	31.3	31.2
15	51.0	45.7	46.5	28.0	26.0
20	48.5	43.4	—	—	24.0
25	46.5	40.8	—	—	—
30	44.0	38.5	—	—	—

These results—which are directly opposed to those obtained with aqueous solutions—are not easy to interpret. The cryoscopic observations of Beckmann⁹⁵ showed a normal molecular weight for each of the alkali chlorides,⁹⁶ so that the ionisation must be accompanied by the production of a single ion for each molecule of chloride added to the solvent. This consideration would rule out the idea of any extensive ionisation according to the equations:



but is consistent with the scheme:



provided that the intermediate complex is almost wholly dissociated⁹⁷ in one direction or the other. This view of the nature

⁹⁴ *Amer. Chem. J.*, 1909, **41**, 451; *A.*, ii, 638. Compare Foote and Levy, *ibid.*, 1907, **37**, 494; *A.*, 1907, ii, 440.

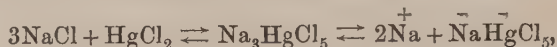
⁹⁵ *Zeitsch. anorg. Chem.*, 1907, **55**, 175; *A.*, 1907, ii, 739.

⁹⁶ Mercurous chloride gave values corresponding closely with the formula Hg_2Cl_2 ; cuprous chloride, values intermediate between CuCl and Cu_2Cl_2 .

⁹⁷ Or that any incomplete dissociation of this complex is balanced by a further dissociation into $2\overset{+}{\text{Na}} + \overset{-}{\text{HgCl}}_4$.

of the ionisation receives strong support from the fact that bivalent barium chloride, which cannot dissociate in this way, is insoluble in fused mercuric chloride, although its solubility in water is much increased by the presence of this salt. Bivalent cupric chloride dissolves, but does not increase the conductivity of the mercury salt.

The rapid increase of molecular conductivity in the more concentrated solutions may be due, (1) as in the case of sodium metaphosphate, to changes in the viscosity of the liquid, or (2) to some new type of ionisation. The author suggests:



but it is possible that the changes observed may be due merely to the decrease by dilution of the autolytic conductivity of the fused sodium chloride.

The work of A. H. W. Aten⁹⁸ on the conduction of electricity in mixtures of metals and their salts appears to be mainly an investigation of the properties of the chloride BiCl. It is of interest to note that whilst the fluidity and conductivity of mixtures containing up to 40 per cent. of bismuth increase together from 260° to 340°, the ratio μ/f shows a steady decrease comparable with those observed by Goodwin and his colleagues.

In conjunction with the observations of Foote and Martin, it is of interest to note that the existence of the complex K_2HgI_4 in aqueous solutions has been clearly established by a variety of methods,⁹⁹ the most recent of which depends on measuring the distribution of iodine between an aqueous potassium mercuri-iodide solution and an organic solvent, such as carbon disulphide or carbon tetrachloride.¹ The results obtained, whilst agreeing with the view that the chief complex is $2\text{KI},\text{HgI}_2$, give indications of the presence of a second complex, either KI,HgI_2 , or more probably $3\text{KI},2\text{HgI}_2$, containing a larger proportion of mercury.

The existence of complex ions in aqueous solutions of cupric chloride and cobalt chloride was advocated some years ago by Donnan and Bassett² as an explanation of the colour changes

⁹⁸ *Zeitsch. physikal. Chem.*, 1909, **66**, 641; *A.*, ii, 537.

⁹⁹ See Abegg, Immerwahr, and Jander, *Zeitsch. Elektrochem.*, 1902, **8**, 688 (solubility of mercuric iodide in aqueous potassium iodide); Sherrill, *Zeitsch. physikal. Chem.*, 1903, **43**, 705; 1904, **47**, 103; *A.*, 1903, ii, 534, 649; 1904, ii, 337 (concentration cells, freezing points of potassium iodide solutions after addition of mercuric iodide, distribution of mercuric iodide between benzene and potassium iodide solutions); Bredig and Walton, *Zeitsch. Elektrochem.*, 1903, **9**, 114; *Zeitsch. physikal. Chem.*, 1904, **47**, 185; *A.*, 1903, ii, 282 (action of mercuric iodide in diminishing catalysis of hydrogen peroxide by potassium iodide solutions).

¹ H. M. Dawson, *Trans.*, 1909, **95**, 870.

² *Trans.*, 1902, **81**, 939.

which these salts undergo on changing the temperature or concentration of their aqueous solutions, or on adding salt or calcium chloride. This view was confirmed by the observations of V. Kohlschütter,³ who showed that the transport-number for copper in aqueous solutions of cupric chloride diminishes as the concentration increases, and finally becomes negative for all solutions stronger than 2.5*N*. These measurements have recently been repeated by H. G. Denham,⁴ who gives the following values:

$N=0.032$	1.163	2.243	3.242	4.300	4.467	5.496
$u/(u+v)=0.405$	0.276	0.221	0.207	0.061	0.007	-0.127

the negative values being very small, and restricted to concentrations above 4.5*N*. Copper bromide, however, gave much more striking results:

$N=0.106$	0.414	1.690	2.218	2.662	3.187	4.055	5.288
$u/(u+v)=0.445$	0.440	0.069	0.052	-0.003	-0.086	-0.159	-0.392
Bluish-green	Green.	Brownish-green.		Brown.		Deep brown.	

the diminution of the transport-number being accompanied by a progressive change of colour from blue to brown. In alcohol the values were:

$N=0.091$	0.321	0.658	0.833	0.863	1.212
$u/(u+v)=-0.165$	-0.245	-0.339	-0.429	-0.460	-0.640

the colour of the solutions ranging from brown to deep brown. Cobalt bromide gave in aqueous solutions:

$N=0.090$	0.459	1.345	2.448	3.106	4.731	5.554
$u/(u+v)=0.409$	0.413	0.340	0.322	0.215	0.005	-0.444

and in alcohol:

$N=0.260$	0.692	0.753
$u/(u+v)=0.102$	-0.121	-0.301

These observations can only be accounted for by the existence of complex anions containing copper or cobalt as well as chlorine. It is pointed out that the simplest complex salts, for example, $\text{Cu}^{++} | \text{CuCl}_4^-$, would give zero values if the ions were equally mobile and positive values if the cation, carrying an equal and opposite charge but not encumbered by chlorine, were more mobile than the anion. Negative transport values might result if the cation were loaded up with water or alcohol, or if the complex salt had a formula of the type $\text{Cu}^{++} | (\text{CuCl}_3)^-$, with twice as much of the metal in the negative as in the positive radicles.

³ *Ber.*, 1904, 37, 1153; *A.*, 1904, ii, 338.

⁴ *Zeitsch. physikal. Chem.*, 1909, 65, 641; *A.*, ii, 373.

Non-aqueous Solutions.

Recent work on non-aqueous solutions has been largely concerned with extending the observations to extreme dilutions, in order to realise experimentally the limiting values of the molecular conductivity.

In the case of ethyl alcohol, this has been done independently by P. Dutoit and H. Rappeport,⁵ and by B. B. Turner.⁶ In the former case, the conductivities were measured at 18°, and the limiting conductivities, reached at about 20,000 litres, were as follows:

KCNS.....	41.1	KI....	39.2	NaI... ..	39.1	NaAc	31.8
(NH ₄)CNS...	38.0	NH ₄ I..	35.0	LiI	35.8	NH ₄ Br ...	36.4

It is claimed that Kohlrausch's law of independent ionic velocities holds good within the limits of experimental error, but that Ostwald's dilution law does not apply. The actual velocities are only about one-half as great as in water, but the ratio varies from 1/1.8 to 1/3 for the different ions.

Turner's observations covered a range of temperature from 0° to 78°, and were extended in one case to an extreme dilution of 452,000 litres. In the case of potassium iodide at 25°, a maximum molecular conductivity (48.5 to 49.5) was reached at a dilution of about 20,000 litres; beyond this lower values were obtained.⁷ In spite of a rise in the temperature-coefficient of conductivity, there is a steady decrease in the coefficient of ionisation as the temperature rises, for example, for *N*/10-potassium iodide the coefficients are 0.49 at 0°, 0.46 at 25°, and 0.35 at the boiling point. The chief source of error at high dilutions was the contamination from glass vessels in which water had been allowed to dry.

E. H. Archibald and W. A. Patrick⁸ have measured the electrical conductivity of alcoholic solutions of iodine and platinum tetraiodide. The former solution became colourless as the conductivity increased, and the electrolyte was probably hydrogen iodide or acetic acid formed in contact with the platinum-black; the conductivity of the platinum salt became constant much more quickly.

Sulphur dioxide has been investigated by P. Dutoit and E. Gyr⁹ at dilutions from 125 to 64,000 litres, the electrolytes being the bromides and iodides of potassium, rubidium, ammonium, and tetraethylammonium. Extreme care was taken to avoid the

⁵ *J. Chim. Phys.*, 1908, **6**, 545; *A.*, 1908, ii, 924.

⁶ *Amer. Chem. J.*, 1908, **40**, 558; *A.*, ii, 13.

⁷ Compare W. C. D. Whetham, *Proc. Roy. Soc.*, 1905, A, **76**, 577; *A.*, 1906, ii, 69.

⁸ *Brit. Assoc. Report*, Winnipeg, 1909.

⁹ *J. Chim. Phys.*, 1909, **7**, 189; *A.*, ii, 461.

formation of sulphur trioxide or sulphuric acid by the action of moisture, air, and light, the dilutions being carried out in closed vessels protected from the atmosphere. The molecular conductivities tended towards a maximum value, although this was not actually reached. Two methods of extrapolation gave concordant values for the limiting conductivities, and these were found to conform to Kohlrausch's law of independent migration velocities. Ostwald's dilution law was found to hold good approximately for dilutions above 8,000 litres.

The observations of E. C. Franklin¹⁰ on solutions in liquid ammonia were carried out in order to determine whether the curious properties of the amines as solvents for electrolytes were reproduced in the parent substance. L. Kahlenburg and O. E. Ruhoff had shown in 1903¹¹ that the molecular conductivity of silver nitrate in amylamine rose from 0.53 (at $v=0.40$ litres) to 1.48 (at $v=1.16$ litres), and then fell on further dilution to 0.002 (at $v=81.6$ litres). For solutions of silver nitrate in ethylamine, F. L. Shinn¹² recorded a steady decrease from $\mu=9.06$ at 0.934 litres to $\mu=2.31$ at 75 litres; a similar decrease was recorded when ammonium chloride was the solute, and a maximum (at 0.87 litres) and subsequent decrease when lithium chloride was used. For solutions of silver nitrate in methylamine, Franklin and Gibbs¹³ obtained the following noteworthy series of values:

$v=0.24$	0.36	0.61	1.22	2.44	4.37	9.72	19.4	38.8	77.5	154.8	309.0	618.0
$\mu=8.14$	17.2	27.0	33.3	31.5	26.9	22.8	20.4	17.8	22.2	26.2	33.3	44.3
			Max.								Min.	

The remarkable curve obtained in plotting μ against $\log. v$ is apparently a general type, of which limited sections only could be traced in the two preceding cases; it shows a maximum at 1.2 litres, followed by a minimum at 39 litres, and a subsequent rise towards a limiting maximum value at infinite dilution; two points of inflexion separate the minimum from the two maxima, although the second inflexion was not reached at the dilutions recorded above. The ammoniacal solutions, the behaviour of which is now described, reproduced this type of curve completely in the case of copper and zinc nitrates and potassium mercuricyanide and amide, which gave:

¹⁰ *Zeitsch. physikal. Chem.*, 1909, **69**, 272; *A.*, ii, 957. Compare Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 277; *A.*, 1900, ii, 382; *J. Amer. Chem. Soc.*, 1905, **27**, 191; *A.*, 1905, ii, 298.

¹¹ *J. Physical Chem.*, **7**, 254; *A.*, 1903, ii, 464.

¹² *Ibid.*, 1907, **11**, 537; *A.*, 1907, ii, 926.

¹³ *J. Amer. Chem. Soc.*, 1907, **29**, 1389; *A.*, 1907, ii, 840.

		Max.	Min.	
Cu(NO ₃) ₂	$v = 0.569$	1.347	9.95	22450.0
	$\mu = 71.7$	99.8	78.2	498.0
Zn(NO ₃) ₂	$v = 0.999$	1.539	15.25	707.2
	$\mu = 98.8$	103.6	86.30	191.0
K ₂ HgC ₄ N ₄	$v = 1.287$	1.999	19.64	4545.0
	$\mu = 187.3$	198.8	159.8	493.1
NH ₂ K.....	$v = 0.1202$	0.2908	4.686	15050.0
	$\mu = 13.33$	19.31	15.14	209.2

The curves for potassium iodide and silver and ammonium nitrates did not show minimum values, although they sagged sufficiently to give rise to well-marked inflexions; the curve for potassium iodide, in particular, only just failed to rise to a maximum and fall to a minimum in normal and decinormal solutions respectively.

These observations are explained on the view that the final rise to a maximum is identical with that observed in aqueous solutions when a salt is completely ionised by the action of a large excess of the solvent. The conductivity of the more concentrated solutions, on the other hand, was attributed by Franklin and Gibbs to the auto-ionisation of the liquefied salt, acting at first in a medium of extreme viscosity, gradually becoming more efficient as the liquid became more mobile, but on further dilution dying down (as in the case of amylamine on account of the insignificant ionising power of the solvent) or giving place to an ionisation effected by the activity of the solvent.

The evidence of a minimum of molecular conductivity in concentrated aqueous solutions is very slight. Such minima have, however, been observed (by correcting for viscosity) in the intrinsic conductivity μ/f of sodium hydroxide and other salts, the rise in concentrated solutions being attributed, as in the work of Franklin and Gibbs, to the "autolytic" conductivity of the liquefied salt in contrast to the "heterolytic" conductivity effected by the interaction of the solute and solvent (see footnote 89, p. 23).

The Dilution Law.

Ostwald's law, $C(1-\gamma) = k(C\gamma)^2$, for the relationship between the concentration, C , of a binary electrolyte and its coefficient of ionisation applies, as is well known, only to weak electrolytes, such as acetic acid. Stronger electrolytes, although of precisely similar type, are represented most accurately by Storch's equation ¹⁴:

$$C(1-\gamma) = k(C\gamma)n,$$

where n is an arbitrary constant the value of which has been

¹⁴ *Zeitsch. physikal. Chem.*, 1896, **19**, 13; *A.*, 1896, ii, 288.

shown by Bancroft¹⁵ to vary in the case of ten strongly dissociated salts from 1.36 for potassium chloride to 1.55 for silver nitrate, but never to rise even approximately to the value 2, which is required by the law of mass-action. Van't Hoff has indeed suggested¹⁶ that the index for all strong binary electrolytes has the value $n = \frac{3}{2}$, and this view has received confirmation from the observations of W. R. Bousfield,¹⁷ that in the case of potassium and sodium chlorides the values of n vary steadily as the solution is diluted, but in each case extrapolate accurately to 1.5 for infinite dilution. The contrast between the theoretical value $n = 2$ and the observed value $n = \frac{3}{2}$, which is thus well established and complete, constitutes one of the most important of the unsolved problems of the theory of electrolytic dissociation.

An even more striking contrast is shown in the recent work of A. A. Noyes and his colleagues¹⁸ on the conductivity and ionisation of polyionic salts at temperatures between 0° and 306°. Having shown that in the case of acetic acid Ostwald's law holds good right up to 306°, they were able to prove that Storch's law could be applied with an index $n = 1.40$ to 1.55 over a similar range of temperature, not only in the cases of sodium hydroxide, hydrochloric acid, nitric acid, and binary salts, such as potassium chloride, silver nitrate, and magnesium sulphate, but also in the case of the tri-ionic salts, barium nitrate and potassium sulphate. Further experiments showed that the same index ranging from $n = 1.40$ to 1.55 could be used also in the case of the tri-ionic salts, $K_2|C_2O_4$, $Ca|(NO_3)_2$, $Ca_2|FeC_6N_6$, and $Ba_2|FeC_6N_6$; the tetraionic salts, $K_3|C_6H_5O_7$ (citrate) and $La|(NO_3)_3$; and the pentaionic salts, $K_4|FeC_6N_6$ and $La_2|(SO_4)_3$.

For these salts, the law of mass-action would indicate $n = 3, 4$, and 5 respectively as the correct indices, instead of the observed values, which are practically constant at 1.5. As the dilution law is the same for all salts and at all temperatures, the conclusion is drawn that "the ionisation of salts, strong acids, and bases . . . is not affected (except in a secondary degree) by chemical mass-action, but is regulated by certain general, comparatively simple laws, fairly well established empirically but of unknown theoretical significance."

Ostwald's dilution law has also been investigated by R. Wegscheider and P. Lux¹⁹ in the case of β -naphthalenesulphonic

¹⁵ *Zeitsch. physikal. Chem.*, 1899, **31**, 188; *A.*, 1900, ii, 186.

¹⁶ *Ibid.*, 1890, **2**, 777.

¹⁷ *Phil. Trans.*, 1906, **A**, **206**, 157; *A.*, 1906, ii, 428.

¹⁸ *J. Amer. Chem. Soc.*, 1908, **30**, 335; *A.*, 1908, ii, 348; *ibid.*, 1909, **31**, 987; *A.*, ii, 854.

¹⁹ *Monatsh.*, 1909, **30**, 411; *A.*, ii, 649.

acid, *p*-toluenesulphonic acid, and their sodium and potassium salts. They show that it can be applied to solutions of these acids up to 0.006*N* strength if the value of μ_{∞} is derived from the conductivity of the salts, or up to 0.016*N* if a fictitious smaller value is taken, but beyond these limits formulæ involving fractional indices must be employed. G. F. White and H. C. Jones,²⁰ on the other hand, in an investigation of the "Effect of Temperature and Dilution on the Conductivity of Organic Acids in Aqueous Solution," have verified the substantial accuracy of the law, not only in the case of the fatty acids, acetic, propionic, and butyric, but of phenylacetic, cinnamic, gallic, benzoic, sulphanilic, salicylic, phthalic, and malonic acids, in the last of which the dissociation constant is one hundred times greater than for acetic acid. The deviations observed in the case of stronger electrolytes are attributed by Wegscheider²¹ to the high concentrations of the ions in strong solutions of such electrolytes. The law is regarded as holding good up to a concentration of 0.03*N*, but this result is only obtained by assuming somewhat arbitrary values for μ_{∞} , and is in direct contradiction to the observations of Bousfield²² on the effect of dilution on the index for sodium and potassium chlorides.

General Theory of Solutions.

One of the most important of recent publications is a monograph on "Hydrates in Solution," by E. W. Washburn,²³ which contains an exceptionally valuable review of recent work on the theory of solutions.

A paper by H. C. Jones,²⁴ on the "Present Status of the Solvate Theory," is restricted to work carried out in the author's laboratory during the past ten years.

T. M. LOWRY.

²⁰ *Amer. Chem. J.*, 1909, **42**, 520; *A.*, 1910, ii, 13.

²¹ *Zeitsch. physikal. Chem.*, 1909, **69**, 603; *A.*, ii, 965.

²² *Loc. cit.*

²³ *Tech. Quart.*, 1908, **21**, 360.

²⁴ *Amer. Chem. J.*, 1909, **41**, 19; *A.*, ii, 221.

INORGANIC CHEMISTRY.

IN a part of the subject, which has practically only one large generalisation to depend upon, it is found difficult to give a general idea of the progress of a year's work. A large number of new facts, of greater or less value, have been accumulated, but how far they will tend to the advance of the general theory it is impossible to say. "Science moves but slowly, slowly, Creeping with invisible steps." Owing to the custom which has grown up of publishing results as soon as any have been obtained, the year's progress seems to consist of small bits of research work, often, it is true, of great importance in themselves, but the significance of which cannot be appreciated without a careful study of what has gone before. In an ideal chemical world, nothing would be published until a complete account of the subject of research could be presented. But, apart from the general question of publishing carefully worked out instalments of a large research, the scramble for priority, happily not common in this country, is often responsible for the appearance of immature work. If papers of this kind were withdrawn by their authors as soon as they found that they could not confirm their results, no great harm would be done. Very frequently, however, the papers are left uncontradicted, to produce great confusion in the mind of the chemical student.

Some attempt has been made in this report to show, under different headings, some general results of the increase of knowledge of particular parts of the subject, but naturally they must be incomplete. More or less isolated facts are given, as in previous years, under the groups in which the principal elements are classified.

In his Presidential Address, Sir William Ramsay¹ gave further results of his experiments on the possible transformation of elements. It was thought that solutions of thorium should, after long standing, give rise to small quantities of helium. Accordingly, 270 grams of thorium nitrate were purified and dissolved in water. The solution was introduced into a flask provided with a well-greased stopcock, and the flask was exhausted repeatedly. It was

¹ *Trans.*, 1909, 95, 632.

kept for three years. After freeing the gas collected from carbon dioxide, nitrogen, hydrogen and oxygen, the residue was tested spectroscopically, but the presence of helium was doubtful. Subsequent experiments led to the same result. It was found, however, that carbon dioxide was present in considerable quantity. A further experiment was made in which the grease of the stopcock was protected from the action of the solution, and still carbon dioxide was found in the solution. Further experiments were made on thorium nitrate, to see if radium emanation would break down thorium into carbon. The gas collected showed the presence of carbon dioxide. Similar experiments with solutions containing other elements of the same family as carbon, namely, silicon and zirconium, also yielded carbon dioxide. A further account of similar experiments by Sir William Ramsay and F. L. Usher² gives a comparison of the amounts of carbon obtained when one cubic millimeter of radium emanation was allowed to act on the various solutions:

Solution of.....	H_2SiF_6 .	$\text{Ti}(\text{SO}_4)_2$.	$\text{Zr}(\text{NO}_3)_4$.	$\text{Th}(\text{NO}_3)_4$.	$\text{Pb}(\text{ClO}_3)_2$.
			I II	I II	
Carbon	0.518	0.982	1.071	0.873	2.93 0.968 0.102 mg.

The emanation was collected from a radium bromide solution containing 0.21 gram of metallic radium, and the amount of emanation used varied from 0.0649 to 0.1120 cubic millimetre. The experimental skill required in working with such exceedingly small quantities is prodigious. It is to be hoped, with the advent of the Radium Institute, that larger quantities of the material may shortly become available, and everyone will look forward with great interest to the repetition of the experiments on a larger scale. A possible source of error in the experiments with thorium nitrate has been pointed out by O. Angelucci.³ It was found that a concentrated solution of thorium nitrate, placed in a dilatometer, showed a considerable increase in volume. After some months, the solution deposited acicular crystals having the composition of $6\text{Th}(\text{NO}_3)_4 \cdot \text{Th}(\text{C}_2\text{O}_4)_2 \cdot 48\text{H}_2\text{O}$. It is suggested that the carbon dioxide evolved from the solutions of thorium nitrate is really produced by the decomposition of the very soluble double oxalate and nitrate of the metal.

In connexion with the production of helium by the breaking down of radium, Sir William Tilden has made a suggestion that the other inert gases, neon, argon, krypton, and xenon, may themselves have been the result of the breaking down of elements of

² *Ber.*, 1909, **42**, 2930; *A.*, ii, 850.

³ *Atti R. Accad. Lincei*, 1909, [v], **18**, i, 526; *A.*, ii, 742.

higher atomic weight than radium. Such elements may conceivably be still present in the earth's crust.

Of the eighty-one elements, no less than twenty-seven have atomic weights which are multiples of unity to the first decimal place, and it is perhaps natural that many chemists believe, although perhaps with reservations, in the truth of Prout's hypothesis. Many attempts have been made of late years to reconcile the hypothesis with facts, of which perhaps the least artificial is the one of A. C. and A. E. Jessup.⁴ Another of these attempts which was, on its publication, received with perhaps a little too much enthusiasm, is that of A. C. G. Egerton.⁵ This author supposes that the divergence of the atomic weights from whole numbers is caused by the excess or defect of electrons. If N is the number of the element in the order of the atomic weights, the accurate atomic weight is given by the formulæ:

For "even" elements, $M = A \pm 0.0978A$, where $A = 2N$.

For odd elements, $M = A \pm 0.0078(A - 1)$, where $A = 2N + 1$.

The weight of an electron is taken as one-thousandth that of an atom of hydrogen, and 0.0078 would represent a group of eight electrons.

For the first twelve elements, the agreement of the calculated numbers with the most recent atomic weight determinations is good. Aluminium and silicon, about the atomic weights of which there may perhaps be some doubt, show a difference of 0.1. For the elements between sulphur and nickel, the above formulæ do not hold, but, by introducing arbitrary factors, agreement between the calculated and observed numbers is obtained.

J. Moir⁶ points out that most of the agreement indicated by Egerton is due to mathematical necessity, and he shows that proof of the hypothesis could only be established if the atomic weights were known to the third place of decimals. Moir himself tentatively advances another hypothesis. He assumes that the fundamental cause of valency in an element of valency n is caused by the presence in it of n atoms of a sub-element of atomic weight 0.0089. Thus the primordial stuff in an atom of hydrogen weighs 0.9989. Sixteen times this weight plus twice the atomic weight of the sub-element gives 16.000 for the atomic weight of oxygen. For thirty-five elements, the difference between the calculated and the usually accepted atomic weights amounts in most cases to less than 0.04. For the remaining atomic weights, an arbitrary number of atoms of a second sub-element of atomic weight 0.1 is assumed. This being done, an agreement of the same order as the first is obtained.

⁴ *Phil. Mag.*, 1908, [vi], 15, 21; *A.*, 1908, ii, 96.

⁵ *Trans.* 1909, 95, 238.

⁶ *Ibid.*, 1752.

One of the difficulties which will strike the readers of the paper will be the different valencies ascribed to similar elements, sulphur, for instance, is diad, and chromium, hexad, but the modesty with which the whole speculation is put forward tends to disarm criticism.

Atomic Weights.

There has been very considerable activity during the year in this branch of chemical work. It is unfortunate that there still remains some doubt as to the exact ratio of the atomic weight of silver to that of oxygen. Nearly three-quarters of the atomic weights depend on this relation, and until it is established there must always be some uncertainty. Many attempts have been made to determine this ratio directly by the analysis of silver oxide, but this substance is difficult to obtain in a pure state. When dried at the highest temperature compatible with safety, it still retains 2.13 per cent. of water. The oxide contains, moreover, less than 8 per cent. of oxygen, and on this account presents extraordinary difficulties as regards its accurate analysis. The chief atomic weight determinations are the following.

Chlorine.—A complete analysis of nitrosyl chloride, NOCl , has been effected by P. A. Guye and G. Fluss.⁷ The weighed substance was distilled over hot silver, which combined with the chlorine; the residual gas was then decomposed by hot copper, which took up the oxygen, and, finally, the nitrogen was absorbed by metallic calcium. The direct ratio of oxygen to chlorine, thus found, was 16 : 35.468. The value for nitrogen found was 14.006. An interesting and valuable paper by R. W. Gray and F. P. Burt⁸ gives the results of the study of hydrogen chloride. The density of this gas was determined and it was also analysed volumetrically. The hydrogen chloride was prepared by three methods: (1) from sulphuric acid and sodium chloride, (2) from sulphuric acid and ammonium chloride, (3) from silicon tetrachloride and water. The gas was solidified and fractionally distilled. In the density determinations, two bulbs were used for measuring the gas, one of soda-glass and one of silica. Both were of comparatively small volume, less than 500 c.c. The gas, having been measured in one of the bulbs, was drawn into an exhausted bulb containing cocoa-nut charcoal cooled by liquid air. The increase in weight of this gave the weight of the measured volume of hydrogen chloride. Special experiments were undertaken to find the volume of gas adsorbed by the surface of the glass bulb. In spite of the great difficulties attending work on a gas so soluble and hygroscopic, very fair concordance was obtained in successive experiments.

⁷ *J. Chim. Phys.*, 1908, 6, 732; *A.*, ii, 135.

⁸ *Trans.*, 1909, 95, 1633.

The second part of the research consisted in the determination of the volumetric composition of hydrogen chloride. This was effected by the use of heated aluminium. Elaborate precautions were taken to ensure the purity of the gas and the absence of volatile impurities in the metal. The agreement of the different experiments was very good. The final result for the atomic weight of chlorine was 35.460, comparing with the value of 35.463 obtained by Dixon and Edgar⁹ in their admirable research on the combustion of hydrogen in chlorine, and with 35.461 obtained later by Edgar.¹⁰ Another paper by O. Scheuer¹¹ deals also with the density of hydrogen chloride. Calculating from his numbers, we obtain the atomic weight of 35.464 for chlorine.

Carbon.—An important paper by A. Scott¹² on the atomic weight of carbon gives an unexpected value for this constant. Carbon has hitherto been regarded as one of the elements which most nearly conform to Prout's hypothesis, having the atomic weight 12.00. Scott, however, finds that this value is at least one-thousandth part too low. The determination was made by the method which is regarded as the most trustworthy of all atomic weight methods, namely, the estimation of bromine by silver. The salts used were tetraethylammonium bromide and tetramethylammonium bromide, and were prepared with the utmost care. They are only very slightly hygroscopic, and, since they are stable up to 150°, there is no difficulty in drying them. The silver used was the same as that used in the estimation of bromine in ammonium bromide. Hence, by subtracting the molecular weight of ammonium bromide from the molecular weights of the tetra-alkyl bromides, values for the molecular weights of two hydrocarbons, C_8H_{16} and C_4H_8 , are obtained. Taking hydrogen as 1.007 and silver 107.88, the values for carbon of 12.019 and 12.017 are found. The individual determinations agree extremely well, and the author seems to have excluded every possible source of error. In order to explain this comparatively large difference between Scott's value and those of Dumas and Stas, Roscoe, Erdmann and Marchand, and others, Sir Edward Thorpe¹³ has drawn attention to a recent paper of P. A. Guye and N. Zachariades.¹⁴ These chemists state that when a very fine powder is weighed, so much air is condensed on it, or occluded by it, that the weight is seriously affected. In the case of finely-powdered potassium chloride, a difference of 32 mg. on

⁹ *Phil. Trans.*, 1905, A, 205, 169; *A.*, 1905, ii, 696.

¹⁰ *Ibid.*, 1908, A, 209, 1; compare *A.*, 1908, ii, 577.

¹¹ *Compt. rend.*, 1909, 149, 599; *A.*, ii, 991.

¹² *Trans.*, 1909, 95, 1200.

¹³ *Proc.*, 1909, 25, 284.

¹⁴ *Compt. rend.*, 1909, 149, 593; *A.*, ii, 989.

100 grams was observed. Scott,¹⁵ in reply, has published a series of experiments on the point. He finds that, with potassium chloride, the difference amounts to only 0.3 mg. on 100 grams, and this error he very reasonably attributes to a hastily constructed counterpoise. The writer made some experiments of the same kind three years ago in connexion with another atomic weight determination. In moist air, all the fine powders tried increased considerably in weight, although the substances were not deliquescent; precipitated silica is a familiar example, whilst in dried air no such increase can be noticed. Hence the increases in weight observed by Guye and Zachariades were probably due to water and not to condensed air.

A new determination of a different kind does not confirm Scott's value. G. Baume and F. L. Perrot¹⁶ have determined the density of highly purified methane. They obtain the number 12.004 for the atomic weight of carbon.

Iodine.—Many chemists have attributed the anomalous position of tellurium and iodine in the periodic classification to an error in the determination of the atomic weight of iodine, since there has always been a possibility that some chlorine was present in the iodine used. Stas, for instance, dried iodine over calcium chloride, and it has been recently shown that some chlorine is set free in these circumstances. In order to exclude the possibility of any element of lower atomic weight being present in the material used, G. P. Baxter and G. S. Tilley¹⁷ have carefully crystallised iodic acid. This was converted by judicious heating into iodine pentoxide, and this reduced by hydrazine. The hydriodic acid was precipitated by silver, and by combining the ratio Ag: I with the ratio Ag: I₂O₅, the atomic weight of 126.891 is obtained for iodine, and the low value of 107.85 for silver.

Tellurium.—The atomic weight of tellurium has been the subject of two researches. V. Lenher¹⁸ has employed the double bromide of potassium and tellurium, K₂TeBr₆. The salt is beautifully crystalline, but it suffers from the disadvantage that it very readily undergoes hydrolysis with water, so much so that Wills, in using the salt for the same purpose in 1879, was compelled to pick out the perfect crystals with forceps. Lenher overcame this difficulty by crystallising from dilute hydrobromic acid, and he found that he could dry the substance satisfactorily without decomposing it. A weighed quantity of the salt was heated in a current of chlorine.

¹⁵ *Proc.*, 1909, **25**, 286.

¹⁶ *Compt. rend.*, 1909, **148**, 39; *A.*, ii, 77.

¹⁷ *J. Amer. Chem. Soc.*, 1909, **31**, 201; *A.*, ii, 225.

¹⁸ *Ibid.*, 20; *A.*, ii, 230.

Bromine and tellurium chloride were expelled, so that the ratio $\text{K}_2\text{TeBr}_6 : 2\text{KCl}$ was obtained. The atomic weight of tellurium, deduced from sixteen very concordant determinations, was 127.55, being still 0.6 above the atomic weight of iodine. P. E. Browning and W. R. Flint¹⁹ have stated that they have separated two distinct substances from tellurium which have the atomic weights 126.49 and 128.85. Their method, the fractional precipitation of tellurium tetrachloride by water, had been previously tried. Baker and Bennett²⁰ found identical atomic weights for the element obtained from the first and the last fractions of the precipitation. In the new work of the two American chemists, two fractions were obtained, one of 50 grams, and the other of 13 grams. The atomic weights were obtained by three methods: (1) Conversion of the basic nitrate into the dioxide, (2) a modification of Brauner's permanganate method, (3) precipitation of the dioxide from the basic nitrate by ammonia and acetic acid. The mean results are, as stated above, 126.49 for the least soluble and 128.85 for the most soluble fraction. Their result, if confirmed, would be of great interest. It may be pointed out, however, that if the mean atomic weight of both fractions is calculated, which would represent the atomic weight of the tellurium before fractionation, it is found to be 126.89, instead of 127.55, as found by other workers. This would seem to indicate that the tellurium originally used had been insufficiently purified, or that the methods used in the atomic weight determinations were not trustworthy. One of the authors is continuing the investigation.

Molecular Weights.

A very considerable amount of work has been done during the year on the determination of molecular weights by cryoscopic and ebullioscopic methods. Since Beckmann²¹ showed that, in all solvents, iodine has the molecular weight corresponding with I_2 , it has been assumed that when the solutions are brown, combination has taken place between the iodine and the solvent. To test this view, experiments have been undertaken²² to determine the freezing-point depression produced by iodine and certain liquids, first separately and then together, in the solvents bromoform and ethylene dibromide. It was found that it was only with liquids which formed brown solutions that the total depression was less

¹⁹ *Amer. J. Sci.*, 1909, [iv], **28**, 347; *A.*, ii, 996.

²⁰ *Trans.*, 1907, **91**, 1849.

²¹ *Zeitsch. physikal. Chem.*, 1907, **58**, 543; *A.*, 1907, ii, 340.

²² J. H. Hildebrand and B. L. Glascock, *J. Amer. Chem. Soc.*, 1909, **31**, 26; *A.*, ii, 225.

than the separate depressions, thus indicating that chemical combination had taken place. The possibility of chemical action between the solvent and the solute compels one to accept with some reserve some recent determinations of the molecular weight of selenium in melted iodine²³ and the similar determinations for the same element dissolved in fused mercuric chloride.²⁴ In the latter solvent, dilute solutions give depressions of the freezing point which indicate variations of the selenium molecule from Se_8 to Se_3 . Similar experiments, with fused mercuric chloride as solvent, gave for sulphur a molecular weight, at all dilutions used, corresponding with S_8 . Tellurium, it is pointed out, does react chemically with the mercuric chloride, reducing it to calomel.

Silent Discharge.

The study of the effect of electric discharge on gases is one of great difficulty, because there is little doubt that the action is complex. The results may be caused by at least three different factors: (1) heat, (2) light, and (3) a specific influence of the electric current, akin to electrolysis in solution. Until comparatively recently the effect was supposed to be due to heat alone, and the increased yield of ozone obtained when the silent discharge was substituted for the spark discharge was ascribed by Brodie to the lower temperature attained. Some experiments by A. Holt, jun.,²⁵ give some help towards the elucidation of the problem as to which of these factors has the most influence. It has already been shown by Dixon²⁶ and by Collie²⁷ that carbon dioxide is decomposed by electric sparks whether it is moist or dry, and that the shorter (and hotter) the sparks, and the lower the pressure of the gas, the greater is the decomposition. It has also been proved²⁸ that ultra-violet light had no effect on moist carbon dioxide, but that the dried gas was decomposed to an extent which varied inversely as the pressure. Holt's experiments show that with the silent discharge there is decomposition in the dried gas to a very considerable extent, 48 per cent. at 30 mm. pressure, and that the extent of the decomposition varies inversely as the pressure. The result in this case thus corresponds with the results of the action of ultraviolet light. In the case, however, of the moist gas, a very striking difference is observed. Instead of there being no action,

²³ G. Pellini and S. Pedrina, *Atti R. Accad. Lincei*, 1908, [v], 17, ii, 78; *A.*, 1908, ii, 833.

²⁴ F. Olivari, *ibid.*, 1909, [v], 18, ii, 94; *A.*, ii, 805.

²⁵ *Trans.*, 1909, 95, 30.

²⁷ *Ibid.*, 1901, 79, 1063.

²⁶ *Ibid.*, 1885, 47, 571.

²⁸ Chapman, Chadwick, and Ramsbottom, *Trans.*, 1907, 91, 942.

considerable decomposition is observed, and this decomposition is greater when the pressure is increased. Unfortunately, no measurements were made of the amount of ozone formed from the liberated oxygen, and until the further experiments are published it would be useless to speculate as to the origin of this very remarkable difference.

It was shown by Brodie²⁹ that in the decomposition of carbon dioxide, dried only by sulphuric acid, as much as 85 per cent. of the oxygen produced was converted into ozone, so that the change $3\text{CO} + \text{O}_3 \rightleftharpoons 3\text{CO}_2$ can scarcely proceed from left to right, a conclusion which was confirmed by the work of Remsen and Southworth.³⁰ Oxygen therefore has little or no oxidising power with regard to carbon monoxide. If, however, other oxidisable gases are passed with oxygen through a silent discharge tube, it has been recently shown that oxidation does take place.³¹ When a mixture of hydrogen and oxygen in the proportion of 2:1 by volume, or with more hydrogen than this, is so treated, water is produced in considerable quantities, but if the oxygen is in excess, no hydrogen peroxide is formed, but only ozone. Chlorine with oxygen gives chlorine monoxide, and hydrogen chloride gives hypochlorous acid. Carbon disulphide is not oxidised by this method, whilst ammonia gives small quantities of hydroxylamine, but no nitrous acid. It is rather remarkable that carbon monoxide and chlorine appear not to react when passed together through an ozoniser.

Combustion.

Notable advances towards the understanding of the theory of combustion have been made by H. B. Dixon and his pupils in recent years. One of the most disputed points in connexion with this work has been the determination of the temperature at which gaseous mixtures undergo inflammation. Experiments by Askenasy and V. Meyer³² gave for electrolytic gas results varying from 518° to 606°, whilst Helier,³³ working with the gaseous mixture passing through a heated tube, obtained 845° as the ignition-point of the same mixture. The variation of the temperatures found is undoubtedly due to the influence of the surface of the vessel used. Most substances act as either positive or negative catalysts, and until this influence could be eliminated or allowed for, no trustworthy results could be expected. By a most ingenious arrange-

²⁹ *Phil. Trans.*, 1874, **164**, 83.

³⁰ *Ber.*, 1875, **8**, 1414.

³¹ E. Comanducci, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], **15**, 15; *A.*, ii, 477.

³² *Annalen*, 1892, **269**, 49; *A.*, 1892, 938.

³³ *Ann. Chim. Phys.*, 1897, [vii], **10**, 521; *A.*, 1899, ii, 85.

ment, H. B. Dixon and H. F. Coward³⁴ have succeeded in igniting the gases out of contact with any solid material. One gas was passed through a wide porcelain tube, which was heated electrically, while the other passed up a narrow tube fixed along the axis of the wide tube. The temperature was measured by a thermo-junction placed either in the narrow tube or just above its orifice. The temperature was gradually raised until ignition occurred, and this ignition took place at a point above the orifice. That the ignition-temperature was not altered by varying the material of the jet was shown by a series of experiments in which fused quartz, Jena-glass, and soda-glass were employed. If the rate of passage of hydrogen through the inner tube, and oxygen through the outer one, was maintained above a certain limiting value, and if the diameter of the outer tube was beyond 40 mm., nearly constant values approximating to 600° were obtained. When air was substituted for oxygen, the very interesting result was obtained that the ignition-temperature was unaltered. For carbon monoxide burning in oxygen, also, the ignition-temperature of 650° was observed, whilst the same gas ignited in air at 651°. The ignition-temperatures of methane, ethane, propane, ethylene, acetylene, cyanogen, hydrogen sulphide, and ammonia were also determined.

A valuable summary of the work done at the Manchester University on the mechanism of the combustion of hydrocarbons was given as a Friday evening discourse at the Royal Institution by W. A. Bone.³⁵ It was shown that the suggestion of H. E. Armstrong, made many years ago, that the combustion of a hydrocarbon takes place through the formation and subsequent decomposition of hydroxylated molecules, has received very considerable experimental support. The preferential combustion either of carbon or hydrogen is an idea which must now be abandoned. By the isolation of large quantities of aldehydic products as the result of the combustion of hydrocarbons at low temperatures, it has been proved that, in these circumstances, Armstrong's hypothesis is well grounded. When the researches were carried on at higher temperatures and under conditions approximating to those in ordinary hydrocarbon flames, it became evident that although the phenomena observed were different, the mechanism of the reaction was essentially the same at high as at low temperatures.

The influence of mere traces of water on the combustion of substances in oxygen and other chemical actions has not yet received an adequate explanation. In 1893 Sir J. J. Thomson³⁶

³⁴ *Trans.*, 1909, **95**, 514.

³⁵ *Nature*, **80**, 82.

³⁶ *Phil. Mag.*, 1893, [v], **36**, 913.

showed that if the force holding atoms together in a molecule were electrical in its nature, the presence of liquid drops of high specific inductive capacity would tend to loosen the bonds between the atoms, and so increase the tendency for chemical action to take place. The difficulty of accepting this explanation was that it seemed impossible that drops of liquid water could exist in a gas containing a very small quantity of water vapour. J. S. Townsend,³⁷ however, has shown that in a gas ionised by Röntgen rays there is a great decrease in the mobility of the ions when a small quantity of water (represented by 0.1 mm. pressure) is present. When more water is added, visible liquid drops are produced. Hence it is probable that with still smaller amounts of water than were present in Townsend's experiments, aggregations of water molecules would be produced if ions existed in the gas, and Sir J. J. Thomson's explanation may hold good. H. B. Baker³⁸ has found that an increase in the ionisation of a mixture of hydrogen and nitrous oxide, at 530°, produces a corresponding increase in the rate of action between the gases. Lime, which has been shown to ionise a gas to a considerable extent, increased the normal rate of union by five times; thoria, which is a much more powerful ionising agent, increased the rate of action by twenty times; whilst with radium bromide the gases exploded directly the temperature of combination was reached. Similar experiments with the carefully dried gases showed that the ionising agents had no effect on the combination of the gases. The hypothesis that, unless water and gaseous ions are both present, chemical union cannot take place, is tentatively advanced.

The Combination of Salts with Water.

The use of salts containing water of crystallisation for atomic weight determinations has been of late years regarded as impossible. Mallet³⁹ pointed out, in regard to the alums, that the water was always in excess of the calculated quantity, and Richards⁴⁰ made a most careful investigation of the water in crystallised barium chloride. In the same circumstances, the excess of water retained was remarkably constant, but by varying the state of division of the salt, large differences were observed. In no circumstances could the theoretical amount of water be obtained. Richards drew the conclusion that no atomic weights with any pretensions to accuracy could be found by using salts which contained water of crystallisation.

³⁷ *Proc. Roy. Soc.*, 1908, **81**, 464.

³⁸ Wilde Lecture, 1909; *Mem. Manchester Phil. Soc.*, 1909, [iii], **53**, 16.

³⁹ Stas Memorial Lecture, *Trans.*, 1902, **81**, 204.

⁴⁰ *Zeitsch. physikal. Chem.*, 1903, **46**, 189; *A.*, 1904, ii, 242.

P. A. Guye and D. E. Tsakalotos⁴¹ assert that it is possible, by working under proper conditions, to obtain the theoretical loss of water from crystallised barium chloride. For this statement they rely on the constancy of the loss experienced on heating the salt. Since, however, they state that the salt was not sufficiently pure for the atomic weight of barium to be deduced, their results must be accepted with some reserve. It may be possible, and it is even likely, that salts with water of crystallisation may be eventually brought into use in accurate work, but until such accurate work is done with highly purified materials, so that atomic weights obtained by their use can be compared with those obtained by unexceptionable methods, the results obtained by the employment of salts with water of crystallisation must be looked upon with suspicion.

The opacity which sometimes makes its appearance in hitherto clear crystals has been investigated in the case of sodium sulphate by D. Gernez.⁴² A 66 per cent. solution of this salt, cooled below 8° in absence of dust, deposits crystals of the heptahydrate, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, and the mother liquor remains supersaturated with respect to the decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. On adding a crystal of the decahydrate, crystallisation occurs through the liquid until it reaches the solid heptahydrate. This then loses its transparency, and becomes opaque. The opacity is ascribed to the formation of decahydrate in the mother liquor occluded in the crystals of heptahydrate. This explanation is supported by the fact that when a fragment of the porcelain-like mass is added to a supersaturated solution of the decahydrate, crystallisation is induced. The facts can be demonstrated in a lecture experiment in the following way. The heptahydrate solution is allowed to crystallise in a U-tube, which has a constriction near the bottom, and the crystals are pressed into a solid cake in the constricted part. On adding a crystal of the decahydrate in one arm of the tube, crystallisation of this hydrate takes place down this arm. When the solid plug is reached, opacity is produced in it, and the formation of the decahydrate proceeds without interruption up the other arm of the tube. The following salts behave in the same way: $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

Since in many cases ammonia seems to be capable of replacing water of crystallisation, molecule for molecule, as in the well-known instances of $\text{CuSO}_4 \cdot 5\text{NH}_3$ and $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, special interest attaches to the compounds which have been prepared of salts

⁴¹ *J. Chim. Phys.*, 1909, **7**, 214; *A.*, ii, 475.

⁴² *Compt. rend.*, 1909, **149**, 77; *A.*, ii, 729.

with hydrazine. Some of these compounds were prepared in 1894,⁴³ such as $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$, $\text{ZnSO}_4 \cdot 2\text{N}_2\text{H}_4$, $\text{ZnCl}_2 \cdot 2\text{N}_2\text{H}_4$, and $\text{CdCl}_2 \cdot 2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. A compound with copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{H}_4$, has also been obtained. In some new experiments,⁴⁴ a large number of salts have been examined in respect of their combination with hydrazine. The substances formed are in general crystalline powders insoluble in water, but soluble in acids and in ammonia. The authors have arrived at the interesting conclusion that one molecule of hydrazine replaces two molecules of ammonia. The hydrazine cannot, as a rule, be driven off from the compounds without decomposing the salts, which may indicate a more definite combination than is supposed to exist between salts and the water with which they crystallise. Comparing the compounds formed with hydrazine with the hydrated salts, the following seem to exhibit a relation: $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 3\text{N}_2\text{H}_4$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{N}_2\text{H}_4$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 2\text{N}_2\text{H}_4$ and $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 2\text{N}_2\text{H}_4$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 2\text{N}_2\text{H}_4$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and others. On the other hand, there are many instances in which this relation does not hold: $\text{BaCl}_2 \cdot 2\text{N}_2\text{H}_4$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 2\text{N}_2\text{H}_4$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. It is probable that a further study of the three types of association which is found between salts and (1) water, (2) ammonia, (3) hydrazine will bring to light facts which will elucidate the very difficult question of the way in which water of crystallisation is connected with the constitution of the salt.

Metals and Alloys.

The very interesting experiments carried on in the University of Utrecht on the breaking up of metallic tin have shown that this metal is not alone in being metastable. Most of the metals in ordinary use are liable to change, although fortunately this change does not commonly take place at the ordinary temperature. E. Cohen and K. Inouye⁴⁵ have shown that if a pattern is etched by nitric acid on a sheet of lead and the sheet kept in contact with another strip at 180° for some hours, the pattern appears on the second strip. Contact under pressure, at the ordinary temperature, does not induce the change. Similar effects have been produced by the contact, at elevated temperatures, between zinc and zinc, brass and copper, copper and copper, and bismuth and bismuth. The metals used had all been rolled out into strips, and therefore had been subjected to severe mechanical strain.

⁴³ Curtius and Schrader, *J. pr. Chem.*, 1894, [ii], 50, 311; *A.*, 1895, ii, 10.

⁴⁴ H. Franzen and O. von Mayer, *Zeitsch. anorg. Chem.*, 1908, 60, 247; *A.*, ii, 40.

⁴⁵ *Chem. Weekblad*, 1909, 6, 881; *A.*, ii, 1008.

A large amount of work has been done on alloys, and in many cases distinct compounds have been isolated, whilst in other cases their existence has been indicated by the form of the freezing-point curves and other methods. A new method has been described for the production of liquid alloys of sodium and potassium.⁴⁶ If potassium is melted in a vacuous Jena-glass flask with sodium hydroxide, and the temperature raised to 250° , a layer of the liquid alloy NaK_2 is formed, even in presence of excess of sodium hydroxide. On similarly treating potassium hydroxide with sodium, the liquid alloy NaK is formed, but on largely increasing the proportion of the hydroxide and raising the temperature to 350° , the alloy NaK_2 is the chief product. G. Masing,⁴⁷ working with metals under pressures of 5000 atmospheres, has come to the conclusion that, contrary to the results of the well-known researches of Spring, pressure has no influence in bringing about the diffusion or combination of metals, but its effect is confined solely to the bringing of the metals into close contact. G. Tammann and Masing⁴⁸ find that after compression the particles of metals can be distinguished by the microscope lying side by side, and combination goes on slowly at the ordinary pressure. For instance, the electrical conductivity of a block of lead and thallium immediately after compression was that of a mechanical mixture of the metals. This increased by 60 to 75 per cent. in the course of a month, showing that combination had taken place.

Group I.

The existence of a true sodium alum, which has been often asserted and denied, has been the subject of an investigation by W. R. Smith.⁴⁹ This author confirms the work of Augé⁵⁰ and Wadmore,⁵¹ and shows that sodium alum forms mixed and layer crystals with other alums. Sodium alum has also been prepared by N. I. Surgunoff,⁵² who shows that the crystals are cubic if they separate from a solution which is supersaturated at 20° or below. Above this temperature the crystals formed are monoclinic.

It is not generally realised how oxidisable solutions of sodium sulphite are in the air. The likelihood of impure material having been used has led to the study of this salt by H. Hartley and

⁴⁶ G. F. Jaubert, *Bull. Soc. chim.*, 1908, [iv], **3**, 1126; *A.*, ii, 41.

⁴⁷ *Zeitsch. anorg. Chem.*, 1909, **62**, 265; *A.*, ii, 669.

⁴⁸ *Zeitsch. Elektrochem.*, 1909, **15**, 447; *A.*, ii, 669.

⁴⁹ *J. Amer. Chem. Soc.*, 1909, **31**, 245; *A.*, ii, 239.

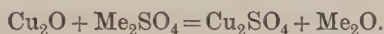
⁵⁰ *Compt. rend.*, 1890, **110**, 1139; *A.*, 1890, 1059.

⁵¹ *Proc.*, 1905, **21**, 150.

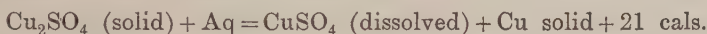
⁵² *Bull. Acad. Sci. St. Pétersbourg*, 1909, 1057; *A.*, ii, 1001.

W. H. Barrett.⁵³ Three forms of the salt have been previously described: Na_2SO_3 , $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$. The authors, working with extreme care, have been unable to confirm the existence of the decahydrate. The crystalline form (hexagonal prisms) of the anhydrous salt has been determined, and the solubility and transition temperature from the heptahydrate to anhydrous salt have been measured.

The long-discussed question of the possibility of the existence of cuprous sulphate has at last been settled by the preparation of the pure salt.⁵⁴ The preparation is carried out by the action of methyl sulphate on cuprous oxide in absence of water:



Ethyl sulphate behaves in a similar way. The action is carried on at a temperature of 160° . The cuprous sulphate is washed with ether, moisture being rigidly excluded, and dried in a vacuum. When dry, the new salt is stable in air, but is decomposed rapidly by water with evolution of heat:



The development of heat in this reaction shows a difference from the behaviour of other cuprous salts, and it explains why the previous attempts to prepare the sulphate in aqueous solution have resulted in failure.

The curiously coloured salt obtained by the action of sulphuric acid on a mixed solution of ferrous and-cupric sulphates⁵⁵ has been examined by A. J. Allmand.⁵⁶ The red colour of the salt changes to chocolate-brown on heating, and finally to mauve. Only a very small quantity of ferric salt is present. The author's experiments lead to the conclusion that the salt is a solid solution of the general composition $(\text{CuFe})\text{SO}_4 \cdot \text{H}_2\text{O}$, but, since the colour of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is pale blue and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is white, the red colour of the combination is still a mystery.

The formula ascribed to the black powder which separates on the anode when silver nitrate solution is electrolysed has been stated to be $\text{Ag}_7\text{NO}_{11}$.⁵⁷ It has been considered⁵⁸ that its formation is preceded by that of a crystalline pernitrate of silver, AgNO_4 . The black powder has been re-examined, and it has been proved that

⁵³ *Trans.*, 1909, **95**, 1184.

⁵⁴ A. Recoura, *Compt. rend.*, 1909, **148**, 1105; *A.*, ii, 579.

⁵⁵ A. Scott, *Trans.*, 1897, **71**, 564.

⁵⁶ *Zeitsch. anorg. Chem.*, 1909, **61**, 202; *A.*, ii, 238.

⁵⁷ O. Šulc, *ibid.*, 1900, **24**, 305; *A.*, 1900, ii, 595.

⁵⁸ G. Baborovský and B. Kuzma, *Zeitsch. Elektrochem.*, 1908, **14**, 196; *A.*, 1908, ii, 378; G. Baborovský and G. Kuzma, *Zeitsch. physikal. Chem.*, 1909, **67**, 48; *A.*, ii, 666.

it consists of a true peroxide of silver, Ag_3O_4 , containing occluded silver nitrate.

Two perborates of potassium have been prepared.⁵⁹ One, which has the formula $2\text{KBO}_3 \cdot \text{H}_2\text{O}$, is obtained by adding cold 3 per cent. hydrogen peroxide solution to a saturated solution of potassium metaborate, KBO_2 . The perborate is precipitated by the addition of methyl alcohol. After standing, the salt is filtered and washed with ice-cold water. It is crystalline and soluble to the extent of 2.5 parts in 100 parts of water at 15° . The dry salt is stable in air, but in water it slowly loses oxygen. The second salt, $2\text{KBO}_3 \cdot \text{H}_2\text{O}_2$, is obtained in a similar way, except that the hydrogen peroxide is of 30 per cent. strength. It is stable in air, but deflagrates when heated to 150° . It is less soluble in water than the former salt. Both the new substances have strong antiseptic properties.

Group IV.

The mixture of gases evolved on treatment of magnesium silicide with hydrochloric acid has been investigated by P. Lebeau. Two hydrides, SiH_4 and Si_2H_6 , were isolated in a state of purity, and a more easily condensable substance, probably Si_2H_4 , was shown to be the source of the spontaneously inflammability of the other two hydrides.

The case for the analogy between silicon and carbon, as regards the formation of chain derivatives, has been summarised by J. Emerson Reynolds.⁶⁰ He makes the interesting suggestion that the function of silicon compounds, which have long been known as constituents of living tissue, is not merely to act as strengthening material, but that they are essential to cell-formation, just as carbon compounds are. The analogy between these two elements has been strengthened by the isolation of what are probably five- and six-silicon-atom chains. A. Besson and L. Fournier⁶¹ have submitted chlorosilicomethane to the action of the silent discharge, and fractionally distilled the resulting liquid in a vacuum. The main products are: (1) $\text{Si}_4\text{Cl}_{10}$, a colourless, oily liquid, which, when decomposed by water, gives a white substance resembling silica in appearance, but emits sparks and ignites when gently rubbed; (2) $\text{Si}_6\text{Cl}_{14}$, a white solid, which melts at 170° , and also gives a combustible substance with water; (3) a solid, yellow mass, soluble in light petroleum, which apparently consists of a mixture of higher chlorides.

⁵⁹ C. von Girssewald and A. Wolokitin, *Ber.*, 1909, 42, 865; *A.*, ii, 312.

⁶⁰ *Roy. Inst. Reports*, 1909.

⁶¹ *Compt. rend.*, 1909, 148, 839; 149, 34; *A.*, ii, 399, 663.

Group V.

Very different compositions have been assigned to the chloride of nitrogen obtained by the action of chlorine on ammonium chloride, many chemists having asserted that it contained hydrogen. The substance, after solution in carbon tetrachloride, has been proved ⁶² to be NCl_3 , direct estimation of hydrogen showing that there is less than one atom of hydrogen to each hundred atoms of nitrogen.

Another chloro-derivative of ammonia has been prepared in a pure state by F. Raschig.⁶³ Equimolecular quantities of ammonia and sodium hypochlorite react according to the equation:



By distilling in a vacuum, a faintly yellow, unstable oil is obtained. This substance, to which the author gives the name of chloroamine, reacts vigorously with alkalis, giving ammonia and nitrogen: black nitrogen iodide is precipitated from a solution of potassium iodide, whilst with ammonia a small quantity of hydrazine is produced. Nitrosyl perchlorate, $\text{NO} \cdot \text{ClO}_4, \text{H}_2\text{O}$, has been prepared by K. A. Hofmann and A. Zedtwitz ⁶⁴ by passing oxides of nitrogen, prepared by the action of nitric acid on sodium nitrite, into perchloric acid. The salt is obtained in colourless, doubly refracting leaflets, which are slightly hygroscopic. Water produces decomposition, resulting in a green solution. Alcohol, ether, acetone, and primary aromatic amines ignite when mixed with the new perchlorate, producing violent explosions.

Although ammonium hydroxide exists in small quantity in a solution of ammonia, the compound has not hitherto been isolated. F. F. Rupert ⁶⁵ has obtained a solid having the composition corresponding with NH_4OH , which is probably a definite compound. The freezing points of solutions of ammonia of concentrations from 4.1 to 100 per cent. have been determined, and the results plotted as a curve, which shows maxima at 49 per cent. and at 65 per cent. The monohydrate should contain 48.6 per cent. of ammonia, and the hydrate, $2\text{NH}_3, \text{H}_2\text{O}$, 65.4 per cent. The behaviour of hydrazine under the influence of different oxidising agents has been studied by A. W. Browne and F. F. Shetterly.⁶⁶ It is shown that the oxidation can proceed in three ways: (1) with formation of fairly large quantities of azoimide and ammonia, when hydrogen

⁶² D. L. Chapman and L. Vodden, *Trans.*, 1909, **95**, 138.

⁶³ *Verh. Ges. deut. Naturforsch. Aertze*, 1907, II. i, 120; *A.*, ii, 232.

⁶⁴ *Ber.*, 1909, **42**, 2031; *A.*, ii, 568.

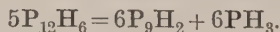
⁶⁵ *J. Amer. Chem. Soc.*, 1909, **31**, 866; *A.*, ii, 726

⁶⁶ *Ibid.*, 221, 783; *A.*, ii, 233, 658.

peroxide, potassium chlorate, or potassium persulphate are used in acid solution; (2) with formation of little or no azoimide but large quantities of ammonia, when the oxidation is effected by potassium permanganate, manganese dioxide, or ferric oxide in presence of sulphuric acid; (3) with formation of little azoimide or ammonia, as is the result of the use of potassium iodate, mercuric oxide, or mercuric chloride. Persulphuric acid gives about 40 per cent. of the possible yield of azoimide, but Thiele's method,⁶⁷ which employs a mixture of hydrazine and ethyl nitrite, is still the most effective.

Continuing his patient study of the nitrites, P. C. Rây⁶⁸ has shown that if a solution of ammonium nitrite is heated in a vacuum very little gas is evolved below 40°; on cooling, most of the salt crystallises. If the temperature is raised to 70°, slow decomposition takes place, but a considerable quantity of the salt appears as a sublimate. There is as yet insufficient evidence to show whether the salt has sublimed unchanged, or whether dissociation and recombination have taken place.

Two new solid hydrides of phosphorus have been prepared.⁶⁹ Calcium phosphide, on treatment with water, gives a mixture which, on passing over granular calcium chloride, gives a yellow deposit. On treatment with cold dilute hydrochloric acid, the calcium chloride is dissolved, and the solid left is washed with water and then with alcohol and ether. The hydride is a canary-yellow powder, which, when first prepared, has no odour. On standing in the air, it rapidly changes, especially in sunlight, giving off a spontaneously inflammable phosphine. It is remarkably insoluble in reagents, and on analysis it is stated to have the composition $P_{12}H_6$. On heating in a vacuum, it turns red and evolves pure phosphine, the residue being the second new hydride,



The second hydride is stable in dry air, but in presence of moisture it is converted into phosphine and phosphoric acid.

Group VI.

The ordinary ozone tube used in the laboratory rarely gives any large percentage of ozone, 3 to 8 per cent. being the usual yield. Chemists will be glad to know of the simple and convenient process described by F. Fischer and K. Bendixsohn.⁷⁰ The ozone is prepared by the electrolysis of dilute sulphuric acid, the anode exposing very

⁶⁷ *Ber.*, 1908, **41**, 2681; *A.*, 1908, ii, 940.

⁶⁸ *Trans.*, 1909, **95**, 384.

⁶⁹ A. Stock, W. Böttcher, and W. Lenger, *Ber.*, 1909, **42**, 2839, 2847; *A.*, ii, 727.

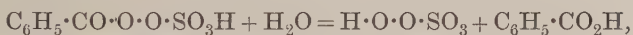
⁷⁰ *Zeitsch. anorg. Chem.*, 1909, **61**, 13; *A.*, ii, 136.

little surface to the liquid. The most effective anode is made by imbedding platinum foil in glass and grinding away the edge so that only a line of 0.1 mm. breadth is exposed. The proportion of ozone in the oxygen evolved amounts to as much as 23 per cent.

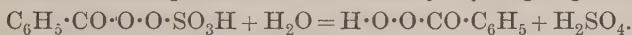
The methods adopted have been hitherto insufficient to decide between the two formulæ assigned to Caro's acid, H_2SO_5 ⁷¹ and $\text{H}_2\text{S}_2\text{O}_9$.⁷² The analysis of salts is inconclusive, since a salt, MHSO_5 , is indistinguishable from $\text{M}_2\text{S}_2\text{O}_9 \cdot \text{H}_2\text{O}$, as in the historic instance of sodium hyposulphite. Two new researches, however, support the former formula, showing that the acid is monobasic. H. Ahrle⁷³ has prepared a nearly pure (92.3 per cent.) acid by the interaction of 100 per cent. hydrogen peroxide and sulphur trioxide. This process was preferred to that of the action of hydrogen peroxide on sulphuric acid, since the equation



was found to be reversible. The experiments show that the acid is monobasic, confirming those of T. S. Price.⁷⁴ The strong acid is stable below 0°, but decomposes slowly at the ordinary temperature. Catalytic agents, such as finely-divided platinum, produce explosive decomposition. R. Willstätter and E. Hauenstein⁷⁵ have prepared the two acyl derivatives, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{O} \cdot \text{O} \cdot \text{SO}_3\text{K}$ and $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{O} \cdot \text{O} \cdot \text{SO}_3\text{K}$. These acyl derivatives are not per-acids, but behave as mixed peroxides of persulphuric acid and acyl. The benzoyl derivative, for example, is decomposed by alkalis into Caro's salt and a benzoate, thus:



and by acids into sulphuric acid and benzoyl hydrogen peroxide:



The acyl derivatives are monobasic acids, and thus the formula H_2SO_5 for Caro's acid is confirmed.

Many chemists have doubted the existence of sulphur dichloride, but the question may be considered as settled by the work of E. Beckmann.⁷⁶ The liquid, produced by the action of chlorine on sulphur monochloride, S_2Cl_2 , can be distilled at low pressures with practically no decomposition. It solidifies at -80° . In solution in liquid chlorine, it has a molecular weight corresponding with the formula SCl_2 , and the same formula is arrived at from cryoscopic

⁷¹ Baeyer and Villiger, *Ber.*, 1901, **34**, 853; *A.*, 1901, ii, 380.

⁷² Armstrong and Lowry, *Proc. Roy. Soc.*, 1902, **70**, 94; *A.*, 1902, ii, 558.

⁷³ *J. pr. Chem.*, 1909, [ii], **79**, 129; *A.*, ii, 395; *Zeitsch. angew. Chem.*, 1909, **22**, 1713; *A.*, ii, 804.

⁷⁴ *Trans.*, 1906, **89**, 53.

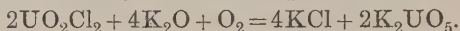
⁷⁵ *Ber.*, 1909, **42**, 1839; *A.*, ii, 566.

⁷⁶ *Zeitsch. physikal. Chem.*, 1909, **65**, 289; *A.*, ii, 137.

measurements in xylene, ethylene dibromide, acetic acid, and bromine.

Many formulæ have been ascribed to perchromic acid. According to E. H. Riesenfeld,⁷⁷ there are two such acids: HCrO_5 , which is blue, and H_3CrO_8 , which is red. These two acids give rise to similarly coloured salts. The molecular weight of the blue pyridine salt has been determined by the cryoscopic method, the solution in water having been used. Since, however, considerable dissociation takes place in this solution, the amount of dissociation had to be separately measured. The molecular weight corresponds with the formula $\text{C}_5\text{H}_5\text{N} \cdot \text{HCrO}_5$. The decomposition of the free acid takes place too rapidly for its molecular weight to be determined. The red potassium perchromate is obtained by the action of chromic acid on a cooled mixture of potassium cyanide and hydrogen dioxide.

On the other hand, W. Oechsner de Coninck⁷⁸ maintains Moissan's formula H_2CrO_5 for perchromic acid, and compares the perchromates with the peruranates which he has obtained by the action of alkalis on uranyl chloride in presence of air, for example:



Group VII.

Nothing can be of more value to the science than the exhaustive study of one particular action. Such a study, if complete, could not fail to throw light on the most difficult of problems, the nature of chemical attraction. The period of induction in the union of hydrogen and chlorine has been investigated by D. L. Chapman and his co-workers for some years past, and it is now certain that the speculation that this period was occupied by the molecules getting up a certain type of vibration must finally be abandoned. It was shown⁷⁹ that a trace of ammonia is responsible for a long induction period. The ammonia would produce nitrogen chloride, which itself strongly inhibits the action. It has also been proved⁸⁰ that, contrary to the statement of Bunsen and Roscoe,⁸¹ excess of either of the reacting gases, hydrogen and chlorine, to the extent of 6 per cent. has no influence on the rate of union. The influence of oxygen as inhibiting the action was first pointed out by Bunsen and Roscoe (*loc. cit.*). Their observation has been confirmed, and from quantitative measurements Chapman and MacMahon⁸² have

⁷⁷ *Ber.*, 1908, **41**, 3941; *A.*, ii, 51.

⁷⁸ *Bull. Acad. roy. Belg.* 1909, 175; *A.*, ii, 318.

⁷⁹ Burgess and Chapman, *Trans.*, 1906, **89**, 1433.

⁸⁰ D. L. Chapman and P. S. MacMahon, *ibid.*, 1909, **95** 135.

⁸¹ *Phil. Trans.*, 1857, **147**, 390.

⁸² *Trans.*, 1909, **95**, 959.

drawn the conclusion that if the relation of oxygen present to the sensitiveness of the mixture, which they have established for small quantities of oxygen, holds with infinitely small quantities of oxygen, then the sensitiveness of pure hydrogen and chlorine would be infinite, in other words, these gases would combine in the dark. Nitrogen, carbon dioxide, and nitrous oxide only act as diluents, whilst nitric oxide acts as an inhibitor. It is pointed out that the inhibiting gases are all capable of reaction with the constituents of the explosive mixture.

Iodine dioxide, obtained first by Millon in 1844, has been prepared in a pure condition by M. M. Pattison Muir.⁸³ By acting with concentrated sulphuric acid on iodic acid until iodine begins to be evolved, and allowing the mixture to cool, a yellow, crystalline crust is obtained. This, after washing with water, and then with ether, gives the pure dioxide of iodine. Owing to its insolubility and its decomposition on heating, its molecular weight could not be found. By the direct action of sulphur trioxide on iodine dioxide, a solid compound, $\text{I}_2\text{O}_4 \cdot 3\text{SO}_3$, was obtained.

A substance which is possibly another oxide of iodine has been obtained by F. Fichter and F. Rohner⁸⁴ by the action of ozonised oxygen on iodine dissolved in chloroform. A yellowish-white precipitate is produced, which is very sensitive to moisture and readily deliquesces to a black syrup. This ready absorption of water seems to distinguish it from the dioxide described above. The percentages of iodine and oxygen determined by the analysis of this product add up to only 97, but on the results of these analyses the authors ascribe the formula I_2O_9 to the substance. There must remain some doubt as to its real constitution until a purer product has been obtained. Chloroform very strongly retained seems to be the impurity.

Group VIII.

The mechanism of the process of the cementation of iron has been long doubtful. Contributions towards the solution of this problem are made in two recent papers. G. Charpy⁸⁵ has shown that iron takes up carbon from carbon monoxide, but whether iron carbonyl was first formed was not investigated. It has been believed that carbon can be taken up directly when heated with iron, but the experiments on which the belief was based have not been unexceptionable. A new series of experiments has been published, in which great care has been taken to exclude the possibility of gaseous

⁸³ *Trans.*, 1909, **95**, 656.

⁸⁴ *Ber.*, 1909, **42**, 4093; *A.*, ii, 991.

⁸⁵ *Compt. rend.*, 1909, **148**, 560; *A.*, ii, 405.

compounds either being present or being formed. Sugar-charcoal, purified by heating in chlorine, was heated with iron to 1000° in a vacuous glazed porcelain tube, the iron being freed from occluded gases by a preliminary heating in a vacuum. In these circumstances, no cementation took place. Since, however, it was possible that the contact of the two elements was insufficient, they were packed into a steel cylinder provided with a finely perforated screw stopper. If the stopper was loose and the cylinder and its contents were heated in the vacuous tube, it was again impossible to find any evidence of union. When, finally, the cylinder was treated in the same way, with the screw stopper exerting great pressure on the mixture, as much as 0.3 per cent. of carbon was taken up by the iron. The conclusion, therefore, must be drawn that under manufacturing conditions, the cementation of iron takes place entirely through the agency of gaseous compounds. The passive state of iron is a phenomenon which, like the rusting of the same metal, seems to be of perennial interest. The existence of a thin film of oxide on iron, which has been rendered passive by any of the well-known methods, has been denied on optical grounds.⁸⁶ It is shown,⁸⁷ however, that by making bright iron the anode in the electrolysis of strong sodium hydroxide, the passive state is induced by the formation of a layer of oxide so thin as not sensibly to interfere with the reflecting power of the surface.

If the force which binds water of crystallisation to salts is distinct from ordinary chemical attraction, the same thing probably applies to the union of substances with hydrogen peroxide. Many compounds have been obtained by means of hydrogen peroxide, in which it is hard to say whether a real peroxidised compound has been prepared, or if the hydrogen peroxide is in a state of association similar to that of water of crystallisation. A peroxide of nickel⁸⁸ has been prepared by the addition of a cooled alcoholic solution of potassium hydroxide to a mixture of nickel chloride and hydrogen peroxide at -50° . It is a greyish-green powder, having the composition $\text{NiO}_2 \cdot x\text{H}_2\text{O}$, which gives all the reactions of hydrogen peroxide, easily liberating this substance when treated with dilute acids. For this reason, the authors believe that it has a different constitution from that of the black nickel dioxide, which is obtained by the action of sodium hypobromite on nickel hydroxide. S. Tanatar,⁸⁹ however, finds that the dioxide prepared by the latter

⁸⁶ W. J. Müller and J. Königsberger, *Zeitsch. Elektrochem.*, 1907, **13**, 659; *A.*, 1907, ii, 924.

⁸⁷ P. Krassa, *ibid.*, 1909, **15**, 490; *A.*, ii, 738.

⁸⁸ G. Pellini and D. Meneghini, *Zeitsch. anorg. Chem.*, 1908, **60**, 178; *A.*, ii, 50.

⁸⁹ *Ber.*, 1909, **42**, 1516; *A.*, ii, 484.

process will reduce potassium permanganate, and will also give hydrogen dioxide when treated with hydrogen cyanide. There are, however, other differences between the substances, and Tanatar regards the greyish-green dioxide as a molecular compound, $\text{NiO}, \text{H}_2\text{O}_2$. At present there is no evidence to show which of the formulæ is the true one.

A new oxide of platinum has been discovered by L. Wöhler and F. Martin.⁹⁰ By the electrolysis of a solution of platinic hydroxide in 2*N*-potassium hydroxide, a golden-yellow crust forms on the anode. This was found to have the composition $\text{K}_2\text{O}, 3\text{PtO}_3$. By the action of cooled acetic acid, the trioxide of platinum was obtained as a brown powder. The trioxide readily loses oxygen, and it slowly liberates chlorine from dilute hydrochloric acid. It is without action on dilute sulphuric, nitric, and acetic acids, whilst concentrated sulphuric and nitric acids convert it into the dioxide. It does not decompose hydrogen dioxide.

H. B. BAKER.

⁹⁰ *Ber.*, 1909, **42**, 3326 ; *A.*, ii, 898.

ORGANIC CHEMISTRY.

THE publication of the Index to the Society's Journal at the same time as the Annual Reports makes it superfluous to attempt an account of all the numerous lines of investigation in organic chemistry which have been pursued during the year, even were such a task possible to accomplish within the limits of a Report. The worker interested in any particular line of inquiry will naturally turn to the index for information as to the work which has been done in connexion with that branch, whilst the Honours student, desirous of following the course of research, is not absolved by the reading of a Report from the duty of consulting the original memoirs. The task of an Annual Reporter is rather that of indicating the main channels into which research is being directed, and the most important theoretical and practical advances made within the period covered, keeping more particularly in view the requirements of those workers in other departments who may desire to know the progress of studies related to, but not directly connected with, their own. Considering, however, the great number and diversity of investigations in organic chemistry, it is inevitable that the full bearing of many should not be discernible until sufficient time has elapsed for them to fall into proper perspective, whilst the incomplete condition and indecisive results of others renders it impossible to summarise them in an adequate manner until further material has been accumulated.

The recent development of research in organic chemistry exhibits evidence of the great influence of the study of physics on the one hand, and of biology on the other. The application of physico-chemical methods to the study of organic compounds is largely responsible for the increasing interest shown in the relation of physical properties to chemical constitution, and in the mechanism of reactions. Whilst the older structural organic chemistry, aiming principally at the synthetical formation of compounds and the determination of constitution, was mainly concerned with the final products of a given reaction, more and more attention is now being devoted to the dynamical aspects of reactions,

embracing the quantitative study of velocity, etc., as well as the molecular mechanism by which the interchange is effected. Intimately connected with such inquiries is the study of the influence of catalytic agents, such as "contact substances" in processes of oxidation and reduction, acids in esterification or substitution by halogens, metallic salts in condensation, and minute quantities of diverse substances in the acceleration of isomeric change.

The chemical importance of certain physical properties, notably colour and fluorescence, in their relation to structure, has been dealt with in several previous Annual Reports. The volume of material is this year even greater, and we are still far from possessing a complete theory of the phenomena. The tendency to employ dynamical hypotheses, rather than to assign to purely statical configurations the power of producing absorption or resonance under the influence of light-waves, continues to be conspicuous in memoirs dealing with this question, but a comprehensive physical explanation is as yet lacking. The formulation of ideas of structure in terms of the electron theory has so far made little progress in organic chemistry, the conception being still too indefinite for immediate application to so complex a problem. A few such attempts have been made during the past year,¹ but it has not been found possible to represent the linkings of atoms by means of electrons in such a way as to secure general acceptance.

Reference was made in last year's Report (p. 74) to the importance of the subject of unsaturation. It is hardly an exaggeration to say that the distribution of residual affinity in the molecule, with all that it implies, is the central problem of organic chemistry at the present time. The influence of unsaturated or double linkings on the properties of a compound, the changes in valency and linking involved in the formation of additive compounds, which so often precedes substitution or exchange of radicles, and the nature of the so-called "partial valencies," are questions which recur in one form or another in investigations dealing with the greatest possible variety of compounds and of reactions. In this direction, also, conspicuous advances have to be recorded.

On the other hand, the influence of biology is seen in several branches of work. Steady progress is being made in the study of substances of bio-chemical importance, the attack being directed from two quarters, namely, the investigation of products obtained by the degradation of complex compounds, and the synthesis of progressively larger and larger molecules with the

¹ J. M. Nelson and K. G. Falk, *School of Mines Quarterly*, 1909, **30**, 179; *A.*, i, 349; B. Flürscheim, *Proc.*, 1909, **25**, 261.

object of reaching the structure of the naturally occurring compound in an upward direction.

The problems concerning the relationship between the chemical properties and the physiological functions of the proteins, polypeptides, cholesterol, lecithin, and other constant constituents of living organisms, are now beginning to assume definite shape, and their solution may soon make rapid progress.

The great interest attaching to the chemistry of the alkaloids, and of such substances as adrenaline, is closely connected with their physiological activity. When a number of derivatives, related to a compound of one of these classes, are studied chemically and physiologically, it is often possible to obtain a relation between a certain type of structure and the exhibition of activity. Valuable as such rules are within the limits of a particular group, there are few broad generalisations applicable to widely different substances. Here, as elsewhere, the mode of distribution of residual affinity in the molecule is evidently of primary importance.

Several researches, of great intrinsic interest, are omitted from this Report on account of the publication, too late to be incorporated fully, of important contributions which can be better discussed, in the light of further research, in the Report for next year. The nature of carbonium and oxonium compounds and the structure of the complex cyanides are among the subjects the discussion of which is thus postponed. Our knowledge of the two colouring matters which infinitely surpass all others in their importance for life, namely, hæmoglobin and chlorophyll, has made great strides during the past year, but the researches so far published are incomplete, and there is some reason to expect that the Reporters for 1910 will be able, in dealing with the whole subject, to record the discovery of the key to the problem.

Some of the more important theoretical advances are considered first, followed by an account of new practical methods and general reactions, and the report closes with a description of recent work in several groups of compounds which have engaged attention during the past year.

Unsaturation.

For a long time it has been recognised that the polar character of a substitutive group influences the whole chemical behaviour of a substance in which it is found. In particular, "negative" groups, or those which as "ions" move towards the positive pole during electrolysis, usually raise the dissociation constant of an acid in which they are present as substituents, whereas "positive" radicles have the opposite effect. Nevertheless, this is not consistently the

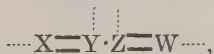
case, and frequently the reverse is noticed. Vorländer² called attention to the fact that the general influence of a group is not merely dependent on its polar character, but also on its state as to saturation. Werner, Michael, Flürscheim, and others have endeavoured to develop views of the affinity values of atomic linkings which combine both these factors, and Werner, from such views, has deduced that elements of decidedly electropositive or negative character will be most definitely affected in their combination by this polarity, whilst those of intermediate character, such as carbon and hydrogen, will act almost independently of such polar character.

Thiele was the first to enunciate in one form the principle that the effect of unsaturation is not merely exhibited in an apparent attraction for external agents, but is also partly exerted on the rest of the molecule. The mutual interaction of such residual affinities in different parts of the molecule tends to alter in a marked degree its external relations, so that, when two points of residual affinity are found in one molecule, the total residual affinity outwardly displayed is not the sum of those which would be exhibited by each in absence of the other. This may be represented in accordance with Werner's suggestion, by imagining that the attractive force of free affinity of any atom is always disposed in part externally, but also in part internally, thus absorbing a portion of the affinity of the atom in its neighbourhood.

For example, if a multivalent atom X is attached to a second multivalent atom Y, and the strength of the bond uniting them is normally represented by 1, then, if X becomes possessed of free affinity either by a change of valency or by becoming one of a pair of doubly linked atoms, part of the resulting free affinity is exerted externally and part internally, so that the bond which attaches it to Y now has a tenacity somewhat greater than 1.

Thus, if the compound $\overset{a}{b} > X - Y < \overset{c}{d}$ becomes $a - X = Y - c$, the result will be that X, in virtue of its unsaturation, exercises some external attractive power, but also binds *a* more firmly than before, the same applying to Y and *c* in their mutual relations.

Thiele's case of the conjugation of double linkings is evidently only a special case of this. Thus, if there were in $X = Y - Z = W$ no internal mutual engagement of the residual affinities, the external effect of the system might be represented as



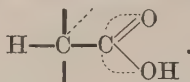
but the subsidiary affinities of Y and Z become partly (or sometimes

² *Annalen*, 1902, **320**, 110; *A.*, 1902, ii, 250.

wholly, when the molecule is symmetrical) mutually engaged, and the system behaves as



Werner explains the replaceability of the α -hydrogen atom in a carboxylic acid³ by assuming that the residual affinity of the carboxyl oxygen absorbs much of the affinity of the carbon atom of the group, which thus but weakly binds the α -carbon atom, the excess affinity of which thus released then becomes disposed externally, and thus attracts substituting agents:

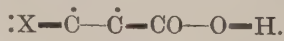


This particular explanation is certainly not satisfactory, and is probably incorrect, as the evidence is all against the assumption that bromine acts directly on the acids, but in favour of the view that the enolic forms of these intervene.

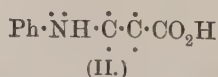
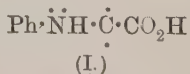
Flürscheim⁴ applies the foregoing principle to the affinities of acids and bases, commencing with the proposition that an unsaturated atom $\ddot{\text{X}}$, replacing a hydrogen atom in the α -position, leads to the following distribution of affinity, in which abnormality in the strength of the linking is indicated by the thickness of the line representing it:



the effect on the ionisable H-atom being to render it less firmly attached to the oxygen, so that this atom is more easily displaced, and the dissociation constant or the affinity of the acid is increased by the presence of $\ddot{\text{X}}$ in the α -position. With $\ddot{\text{X}}$ in the β -position, the reverse would hold true:



This holds good with the anilino-fatty acids, in which (although aniline is basic in character) the α -anilino-derivatives (I) are stronger than the unsubstituted acids, whilst the β -anilino-derivatives (II) are weaker:



Similarly, among unsaturated isomeric acids, the $\alpha\beta$ -derivative is the strongest.

³ *Vierteljahrschr. Züriche. Naturf. Ges.*, 1891.

⁴ *Trans.*, 1909, **95**, 718.

In this sense to halogen atoms and oxygen as well as to tervalent nitrogen is ascribed an unsaturated function capable of manifesting itself in this manner, and generally the magnitude of the effect thus exerted is termed the "quantitative factor."

The replacement of hydrogen by another atom or group will, it is suggested, produce an effect dependent on the "quantitative factor," and also on the polar character of the atom or group, and these may mutually assist or oppose one another according to circumstances, and in particular to their relative positions. Thus, *m*-hydroxybenzoic acid is stronger than benzoic acid, but *p*-hydroxybenzoic acid is weaker.

The order of the groups as to their "quantitative factors" is arrived at by considering their orientating influence on substitution when they are directly attached to a benzene nucleus. Such a preliminary classification of groups is given.

To estimate relative polarity, consideration is taken as to the effect of groups on the affinity of substituted benzoic acids. In the meta- and para-isomerides, steric influence is of little effect, and in these two positions the quantitative influence has opposite effects; the polar effect, on the other hand, is not inverted in this manner, so that when the influence of a group in the meta-position is $p+q$, in the para-position it is approximately $p-q$; one-half the sum $\frac{p+q+p-q}{2}=p$ is therefore a fairly good measure of the polarity of the group.

The results thus obtained render it feasible to estimate, by a consideration of the rates of esterification of acids, the relative sequence of groups on their steric effects, and a preliminary table for these is given.

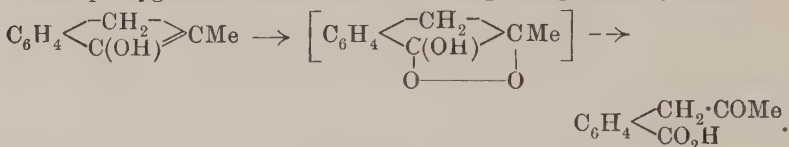
Finally, the author applies his numerical data to foretell qualitatively the effect of the replacement of hydrogen by numerous atoms and groups on the affinities of acids and bases, and with more than ordinary success; in one of the few cases where his conjectures were not in harmony with previous measurements a redetermination of the affinity constant confirmed his prediction.

Whilst many of the author's data are arrived at by theoretical assumptions which may finally prove to be invalid, it must be admitted that in their application, at least to the cases dealt with, they lead to conclusions which are wonderfully near the truth, and the paper should stimulate a very general interest in some of the purely theoretical aspects of organic chemistry.

Only a few of the many other contributions to the study of compounds containing unsaturated linkings can be mentioned. The formation and decomposition of ozonides has been utilised by

a number of investigators as a means of determining the nature and position of double linkings in the molecule. The simplest representative of the class, ethylene ozonide, has been prepared by the action of ozonised air on dry ethylene at -70° , and proves to have the simple formula: $\begin{array}{c} \text{CH}_2 \cdot \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{O} \end{array} > \text{O}$. It undergoes decomposition

with water in two different ways, yielding, on the one hand, formaldehyde and hydrogen peroxide, and, on the other, formaldehyde and formic acid.⁵ It is probable that ordinary oxygen sometimes attaches itself to double linkings in the same way as ozone. Thus the atmospheric oxidation of β -methylhydrindone to phthalic and benzylmethylketone-*o*-carboxylic acids is best explained⁶ by assuming that the enolic form of the ketone takes up oxygen, and that the O·O linking is ruptured by water:



The ketonic acid then undergoes in part a similar rearrangement and oxidation, the products being phthalic and acetic acids.

An important test of the validity of Thiele's law of addition to conjugated double linkings is afforded by the study of the dibromide of *s*-diphenylbutadiene: $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_5$. Thiele's theory led him to regard the dibromide as symmetrical, but some of the reactions of the compound having led to doubt on this point, the oxidation by means of ozone was undertaken.⁷

The products proved to be dibromocinnamaldehyde and benzaldehyde, proving the bromine atoms to be in the $\alpha\beta$ - and not in the $\alpha\delta$ -position. It will appear that whilst the addition of hydrogen always follows Thiele's rule, that of bromine is equally likely to occur at a double linking without shifting of bonds. It is therefore necessary to determine the constitution of the dibromide in each individual case. Nitrogen peroxide follows Thiele's rule,⁸ that is, it is added in the $\alpha\delta$ -position. It is suggested that the addition of H and NO_2 takes place in single radicles, whilst that of bromine takes place primarily in the form of molecules, Br_2 .

The addition of hydrazine and hydroxylamine to unsaturated acids has also been studied,⁹ and whilst it was found impossible

⁵ C. D. Harries and R. Koetschan, *Ber.*, 1909, **42**, 3305; *A.*, i, 755.

⁶ A. H. Salway and F. S. Kipping, *Trans.*, 1909, **95**, 166.

⁷ F. Straus, *Ber.*, 1909, **42**, 2866; *A.*, i, 638.

⁸ H. Wieland, *Annalen*, 1908, **360**, 299; *A.*, 1908, i, 517.

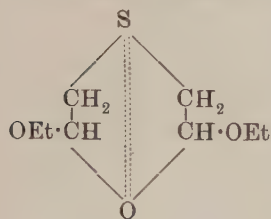
⁹ A. Riedel and E. Schulz, *Annalen*, 1909, **367**, 14; T. Posner and K. Rohde, *Ber.*, 1909, **42**, 2785; *A.*, i, 581, 649.

to obtain an additive compound from hydrazine and cinnameryl-acrylic acid or ester, hydroxylamine was readily added in the $\alpha\beta$ -position:



If we consider the carbon atoms only, addition according to Thiele's rule would occur in the $\beta\gamma$ -position. The observed reaction is, however, in accordance with the rule if we take into account the carbonyl group, addition taking place at the middle linking, not of the group $\cdot\text{C}:\text{C}:\text{C}:\text{C}\cdot$, but of the equally conjugated system $\cdot\text{C}:\text{C}:\text{C}:\text{O}$. This type of reaction is now under systematic investigation.

Diethoxythioxan behaves as a conjugated compound, closely resembling thiophen.¹⁰ Its low additive power distinguishes it from the open-chain sulphides, and even suggests steric hindrance, which is, however, excluded. The known mutual influence of atoms in the 1:4-position suggests that the residual valencies of the oxygen and sulphur atoms saturate one another across the ring, thus accounting for the low reactivity.



The stability of the linking between carbon and amidic nitrogen is greatly affected by the neighbourhood of an ethylenic linking. When this is immediately adjacent, $\text{C}:\text{C}:\text{N}$, the $\text{C}:\text{N}$ union is more easily ruptured on reduction, unless the $\text{C}:\text{C}$ group forms part of a benzene or similar ring. When the double linking is one step removed, $\text{C}:\text{C}:\text{C}:\text{N}$, either an open-chain or a benzenoid linking suffices to facilitate the rupture, but in the former case only if the unsaturated group is a large one, such as cinnamyl, a small group, such as allyl, being without influence.¹¹ Thus, aniline is unaffected by reducing agents, cinnamyltrimethylammonium chloride and sodium amalgam yield phenylpropylene and trimethylamine, whilst trimethylallylammonium chloride is unchanged.

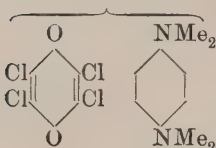
Colour and Constitution.

The problem of the colour of organic compounds is so intimately connected with that of the distribution of unsaturated linkings in the molecule that its consideration may follow at this point. A marked feature of the year's work on the constitution of coloured substances has been the attention devoted to additive compounds,

¹⁰ H. T. Clarke and S. Smiles, *Trans.*, 1909, **95**, 992.

¹¹ H. Emde, *Arch. Pharm.*, 1909, **247**, 314, 333, 351, 369; *A.*, i, 708, 709.

particularly to those of the quinhydrone type. As regards the quinhydrones, the hypothesis proposed by Willstätter,¹² which assumes an oscillatory interchange of quinonoid linkings between the two components of the molecular compound, must now be regarded as untenable, coloured compounds having been obtained in cases where such oscillations are completely excluded. Thus, tetrachloro-*p*-benzoquinone forms strongly coloured quinhydrones



with quinol dimethyl ether and with tetramethyl-*p*-phenylenediamine.¹³ There is here no possibility of interchange.

p-Benzoquinone and *p*-benzoquinonedi-imine form many coloured compounds of similar type with benzidine and other diamines. Fluorenone resembles the quinones in yielding a coloured additive product with *p*-phenylenediamine. The additive compounds of quinones with a single equivalent of monohydric phenols are also coloured.¹⁴

Werner¹⁵ regards the picrates of hydrocarbons as compounds of the quinhydrone type, in which the residual affinity of the nitro-group plays the same part as that of the quinone oxygen atoms, and there is no rearrangement of the nitro- to an *isonitro*-group. Trinitromesitylene yields coloured compounds with aniline and alkylanilines, and even such simple nitro-compounds as chloropicrin, $\text{CCl}_3\cdot\text{NO}_2$, and tetranitromethane are capable of forming similar molecular combinations. Labile hydrogen is, of course, absent in these cases. The depth of the colour increases in the hydrocarbon series from benzene to anthracene, thus following the same order as the picrates. Tetranitromethane may even be employed as a reagent for the detection of double carbon linkings, as it gives distinct yellow colorations with unsaturated aliphatic hydrocarbons. The β -unsaturated acids respond to the test, but not their α -isomerides.

Addition to nitrogen takes place in certain cases, trimethylamine, for instance, giving a brown coloration with tetranitromethane. Hydrazones are also capable of forming coloured additive products with polynitro-compounds, provided that the residual affinity of the nitrogen is not too much reduced by the presence of negative groups. Thus, the phenylhydrazone and phenylmethylhydrazone of piperonaldehyde yield stable, coloured compounds with picramide or picryl chloride.¹⁶

An oscillation of linkings between the acid or basic groups was

¹² *Ann. Report*, 1908, 124.

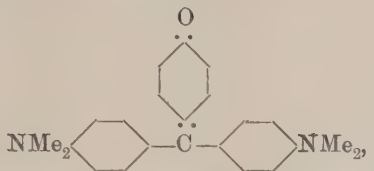
¹³ W. Schlenk, *Annalen*, 1909, **368**, 271, 277, 295; *A.*, i, 807, 808.

¹⁴ K. H. Meyer, *Ber.*, 1909, **42**, 1149; *A.*, i, 395.

¹⁵ *Ber.*, 1909, **42**, 4324; *A.*, 1910, i, 20.

¹⁶ R. Ciusa, *Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 100; *A.*, i, 737.

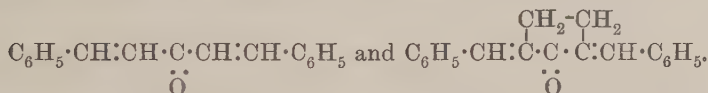
proposed by Baeyer¹⁷ to account for the colour of the triphenylmethane dyes. Schlenk has put this suggestion to the test by preparing *p*-tetramethyldiaminofuchstone,



which proves to be a true dye, and not merely a quinhydrone, although oscillation of the kind proposed by Baeyer is impossible.

A further argument against Baeyer's oscillation hypothesis is afforded by the fact that the trimethyl ether of tetrachlorogallein, although precluded by its formula from exhibiting such oscillatory interchange, nevertheless forms coloured salts and esters.¹⁸

The influence of conjugated double linkings on colour has been studied in an extensive series of unsaturated ketones and their salts.¹⁹ The parent substances chosen for comparison are distyryl ketone and dibenzylidenecyclopentanone:



The introduction of the ring has the expected effect of deepening the colour (shifting the absorption band towards the red) to an extent which is practically equal in all the derivatives examined. The replacement of hydrogen atoms in the phenyl residues by alkyl or alkyloxy-groups causes a change in the same direction, whilst an increase in the length of the chain of conjugated linkings, by the replacement of benzylidene by cinnamylidene, greatly deepens the colour. Furyl has a greater effect than phenyl.

Compounds closely resembling the triphenylmethane derivatives are obtained when one or more of the phenyl groups in the latter are replaced by diphenyl residues.²⁰ The methane linking is in all cases in the para-position, and the colour is progressively deepened by the substitution of diphenyl for phenyl, triphenylcarbinol salts being yellow, and tridiphenylcarbinol bluish-red, the intermediate members being yellowish-red and red. This fact is used by Schlenk as an argument against the representation of the dyes as quinonoid,

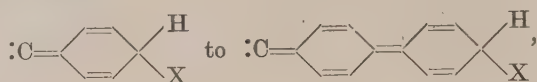
¹⁷ *Ann. Report*, 1907, 117.

¹⁸ W. R. Orndorff and T. G. Delbridge, *Amer. Chem. J.*, 1909, 42, 183; *A.*, i, 733.

¹⁹ H. Stobbe, *Annalen*, 1909, 370, 93; *A.*, 1910, i, 43.

²⁰ Schlenk, *loc. cit.*

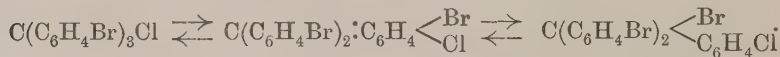
as an abrupt change of colour, such as might be expected to occur on passing from



is not observed.

Further evidence has been brought forward for the view that the yellow solutions of triphenylmethyl contain a quinonoid modification. Gomberg and Cone's important paper²¹ appeared too late to be discussed here, and will be mentioned later in connexion with the general nature of carbonium and oxonium salts.

A solution of tri-*p*-bromotriphenylmethyl chloride in liquid sulphur dioxide yields, after some time, a colourless solid solution of the original substance and 4-chloro-4': 4''-dibromotriphenylmethyl bromide.²² The occurrence of this change indicates an intermediate formation of a quinonoid compound:



The existence of two isomeric triphenylmethyl magnesium chlorides, however, seems to be definitely disproved.²³ All the reactions of the magnesium compound, with the exception of that with aldehydes, lead to a homogeneous product, and this reaction is valueless for such purposes, as even the reaction between magnesium benzyl chloride and formaldehyde is found to take place in two ways, yielding both benzylcarbinol and *o*-tolylcarbinol.

Triphenylmethyl chloride forms coloured additive compounds with phenols, a study of which has led to the suggestion²⁴ that in triphenylmethyl the free valency of the carbon atom unites with the centric valencies of the benzene rings, destroying their symmetry and producing colour.

The variety of formulæ proposed for the phthaleins and their salts is very great, and the insufficiency of any statical formula to represent all the colour-relations of the substance is well seen in this class. S. F. Acree and E. A. Slagle,²⁵ after reviewing the quinonoid and other formulæ, and the hypotheses of oscillating linkings and of coloured free ions, consider them all to be unsatisfactory, and prefer to regard the coloured salts as analogues of the quinhydrone. Instead, however, of leaving the exact nature of the reciprocal influence of the quinone and phenol groups an

²¹ *Annalen*, 1909, **370**, 142; *A.*, 1910, i, 55.

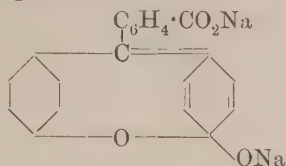
²² M. Gomberg, *Ber.*, 1909, **42**, 406; *A.*, i, 144.

²³ A. E. Tschitschibabin, *ibid.*, 3469; *A.*, i, 778.

²⁴ A. von Baeyer, *ibid.*, 2624; *A.*, i, 641.

²⁵ *Amer. Chem. J.*, 1909, **42**, 115; *A.*, i, 650.

open question, as has been done by several recent workers on the quinhydrones, these authors propose the following formula for the coloured salts of phenolphthalein:



Reference has been made in the last two Annual Reports to the numerous instances of compounds yielding two or even more differently coloured series of metallic salts. In many of these cases there is some uncertainty as to whether the difference is due to true chemical isomerism, or to the more subtle polymorphism, such as is met with in the red and yellow modifications of mercuric iodide. Although a complete molecular explanation of colour must undoubtedly account for even such cases, they are incapable of expression by the ordinary structural formulæ. The numerous structural differences assumed to exist between two series of differently coloured alkali salts of the same compound are, as a rule, unsupported by chemical evidence, and rest only on the observed fact of a physical difference.

Some further interesting observations have been made in this class.

The *o*-nitrophenols are known to give both red and yellow salts with alkalis. The salts with organic bases are, however, all yellow, and have nearly the same shade of colour, whilst the red alkali salts vary greatly. The yellow alkali salts are labile, and yield orange equilibrium mixtures in solution.²⁶

Colourless compounds, such as ethyl 2:4:6-trinitrophenyl-malonate, yield coloured compounds with sodium ethoxide, which exist in a labile and a stable form.²⁷ As the additive compound from nitroanthracene is colourless, it appears that, as in previous instances, two nitro-groups must be in some way involved.

The cyclic oximinoketones, of which violuric acid is a type, present an extraordinary complexity in the colour of their metallic derivatives. The colourless esters must be derivatives of ψ -violuric acid, but two series of coloured salts may be obtained. The changes of colour due to changes of temperature, solvent, etc., have been investigated in a great number of cases.²⁸

²⁶ A. Korezyński, *Ber.*, 1909, **42**, 167; *A.*, i, 148.

²⁷ A. Hantzsch and N. Picton, *ibid.*, 2119; *A.*, i, 467.

²⁸ A. Hantzsch, *ibid.*, 966; A. Hantzsch and P. C. C. Isherwood, *ibid.*, 986; A. Hantzsch and B. Issaïas, *ibid.*, 1000; A. Hantzsch and W. Kemmerich, *ibid.*, 1007; *A.*, i, 331, 333, 335, 336.

The salts of violuric acid with organic amines are either blue or red, mixed salts often being obtained.²⁹ One modification is frequently labile, but there is no rule governing the direction of the spontaneous change, sometimes the blue and sometimes the red salt being the stable form. Violuric acid is coloured in solution, and not colourless, as described by Hartley. The colourless ψ -acid is present in increasing quantity as the temperature of the solution is lowered.³⁰

The methiodides of many cyclic bases are coloured, although the bases themselves are colourless. Hantzsch, from observations of the colour of substituted acridonium and pyridinium compounds, concludes³¹ that the colour is due to the formation of complex molecules, probably united by means of the iodine atoms. Thus, 5-phenyl-10-methylacridonium chloride is only slightly yellow, and proves to be unimolecular in chloroform solution, whilst the blackish-brown iodide is termolecular. The differences of colour persist in the solid state, and occasionally modifications having a different colour may be isolated in a labile form. Similar observations have been made with pyridine methiodide, which is strongly coloured and termolecular in chloroform solution,³² and with the methiodide of ethyl cinchonate, which is red, becoming yellow on taking up water of crystallisation.³³ The reduction of a pyridine ring to piperidine causes the disappearance of the colour.

Mechanism of Chemical Change.

Succeeding a period of many years when the systematic study of this aspect of organic chemistry was confined to a few schools, a great change is noticeable, and organic chemists can no longer be reproached with neglect of this side of their subject. Many of the theories recently advanced are doubtless open to the criticism that they are highly speculative, but this is inevitable in a new subject so shrouded in obscurity, and the amount of harm that may sometimes be done by an erroneous theory is usually outweighed by the stimulus to research which is given by a happy hit. A problem is frequently unsolvable by direct attack, but satisfactory guiding principles may often be arrived at by indirect means, or by a process of trial and error.

The question of the mechanism of homogeneous catalysis by acids is perhaps an example of such a problem, and this appears to be

²⁹ T. Zerewitinoff, *Ber.*, 1909, **42**, 4802.

³⁰ F. G. Donnan and W. Schneider, *Trans.*, 1909, **95**, 956.

³¹ *Ber.*, 1909, **42**, 68; *A.*, ii, 198.

³² C. K. Tinkler, *Trans.*, 1909, **95**, 921.

³³ H. Decker and P. Remfrey, *J. pr. Chem.*, 1909, [ii], **79**, 339; *A.*, i, 408.

yielding, although very gradually, to combined attack from all points. In connexion with that section of it which deals with the mechanism of esterification in alcohol, the largest proportion of credit for recent advances must be assigned to H. Goldschmidt, whose work shows that this phenomenon is the exact counterpart of ester hydrolysis in water, and, so far as the catalyst only is concerned, is mainly or wholly dependent on the ionised part of it. In view of this result, it is impossible to follow Michael's³⁴ contention, that the non-ionised molecules of the catalyst form the intermediate complexes. All workers at this subject are probably agreed that at an intermediate stage the catalyst, or part of it, forms a reactive complex, but it is not yet agreed whether it is with the alcohol or the carboxylic acid in the first instance. It is easy to show that kinetic experiments cannot distinguish between these two possibilities, and the problem will no doubt be solved by less direct evidence, such as the following.

Acids act as catalysts at the ordinary temperature in innumerable reactions in which carbonyl compounds take part, and accelerate, or even bring about, a variety of changes in which aldehydes and ketones as well as carboxylic acids and esters take part. Acetylation by acetic anhydride is greatly aided by traces of mineral acids, and this applies to the acetylation of amines³⁵ as well as alcohols, and the function of the catalyst is doubtless similar in all these cases, but the significant feature here is the observation made by Miss Smith and Orton that it is only with the weak bases that the accelerating effect of the catalyst is marked; broadly, in other words it appears that the greater the opportunity for ammonium salt formation, the less is the influence of the catalyst. It is hardly reasonable, therefore, to suppose that a salt of the amine is a necessary stage, and the only alternative is the initial formation of a compound of catalyst and carboxylic acid. The analogy between ammonium and oxonium salts (salts of amine and alcohol) suggests that the same conclusion holds true in the case of esterification. In this connexion it is noteworthy that Michael considers that in esterification brought about by acid catalysts, the velocity of reaction is conditioned by the affinity between these and the carboxylic acid.³⁶ In view of this opinion and Goldschmidt's experiments, there is some hope that a general agreement is near at hand. Direct proof is still wanting, however, that carboxylic acids form ionisable complexes with mineral acids, and the aid of physical

³⁴ *Ber.*, 1909, **42**, 310; *A.*, ii, 219.

³⁵ Miss A. E. Smith and K. J. P. Orton, *Trans.*, 1909, **95**, 1060; J. J. Blanksma, *Chem. Weekblad*, 1909, **6**, 717; *A.*, i, 779.

³⁶ A. Michael, *Ber.*, 1909, **42**, 310; *A.*, ii, 219.

chemists must be invoked to suggest methods for deciding this question.

Attention has repeatedly been drawn to the fact that the process of direct esterification differs in many respects from the same phenomenon when effected by the agency of a catalyst, and is doubtless regulated by a different mechanism.³⁷

The velocity of formation of carbamide from ammonium cyanate in aqueous solution was shown by Walker and Hambly to be proportional to the product of the concentrations of the ammonium ions and of the cyanate ions: $\text{NH}_4^+ + \text{CNO} = \text{CO}(\text{NH}_2)_2$. The specific inductive capacity of the medium in which the transformation occurs, however, is found to have no obvious effect on the velocity, and it is suggested that the reaction occurs between free ammonia and free cyanic acid.³⁸ This view certainly leads to the same expression for the reaction velocity:



and brings the reaction into line with the cases where an amine acts on alkyl- and aryl-carbimides, as ionisation of the latter is excluded.

α -Halogen substituted fatty acids are converted into the corresponding hydroxy-compounds by water, and the evidence indicates that it is mainly the undissociated part of the acid which is attacked by the water molecules. On the other hand, when the sodium salts are altered by water or alkali, it appears to be the anion which is mainly concerned, and here alkalis appear to be little more efficient than water itself. This is attributed to the circumstance that similar electrical charges on the anion and the hydroxyl ion result in a mutually repulsive effect. Silver salts in aqueous solution also attack the members of this group of acids, and, as in other cases, their behaviour is abnormal. Results such as these promise to throw light on the mechanism of halogen displacement, and in particular on the Walden inversion.³⁹

Alkyl iodides act on the anion of sodium thiosulphate, and the order in reactivity of the halogen compounds corresponds with that observed when they act on ethyl sodioacetoacetate, trimethylamine, and sodium ethoxide; in other words, the reaction belongs to the first type of Donnan and Miss Burke's classification. It is considered possible that the iodides may exist in two molecular states, but no definite suggestions as to the nature of these are made.⁴⁰

³⁷ A. Michael, *Ber.*, 1909, **42**, 310; *A.*, ii, 219; A. Michael and K. J. Oechslin, *Ber.*, 1909, **42**, 317; *A.*, ii, 220; H. Goldschmidt, M. Asriel, V. K. Lund, and O. Udby, *Zeitsch. Elektrochem.*, 1909, **15**, 4; *A.*, ii, 129.

³⁸ A. Michael and H. Hibbert, *Annalen*, 1909, **364**, 129; *A.*, i, 214.

³⁹ G. Senter, *Trans.*, 1909, **95**, 1827.

⁴⁰ A. Slator and D. F. Twiss, *ibid.*, 93.

The substances which undergo the phenomenon known as isomeric change may be divided into two classes, the first comprising those in which the migrating atom or group cannot be shown to be readily separable from the remainder of the molecule undergoing the change, and the second those in which there is evidence of a possible divorce of the mutually labile portions of the molecule during the transformation. In the first category may be placed the Hofmann reaction and allied changes, the Beckmann change, the migration of alkyl groups in the pinacolin and similar transformations; and in these cases the failure of all efforts to discover any separate existence of the migratory groups leads naturally to the supposition that here true intramolecular changes of structure take place; at least the burden of proof must rest with those who would deny the justness of this conclusion.

The azoimides of acids yield carbimides and nitrogen when heated, the first published instance⁴¹ of this transformation being that of cinnamoylazoimide into cinnamenylcarbimide:

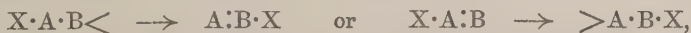


and other cases⁴² have since been described.

To convert an acid into the carbimide, it is often only necessary to heat the acid chloride in an indifferent solvent with commercial sodium azoimide until nitrogen ceases to be evolved.⁴³

The formation of alkylcarbimides from bromoamides and acid azoimides suggests the possibility that nitrile oxides are intermediate products, but in the opinion of those who have investigated this question such a view is not tenable.⁴⁴

The wandering of a group from one atom to the adjacent one suggests a change of two units in the valency of one of the latter at the stage where migration occurs:



and this hypothesis, although in no case an indispensable one, is now frequently invoked in explanation of such changes. Thus Stieglitz's plan for the Hofmann reaction is:



In excellent accord with such a proposition is the transformation of azibenzil (I) and of the sodium derivative of desyl chloride (II)⁴⁵ into diphenylketen:

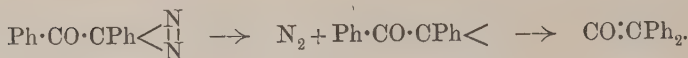
⁴¹ M. O. Forster, *Trans.*, 1909, **95**, 433.

⁴² G. Schroeter, *Ber.*, 1909, **42**, 2336; *A.*, i, 617; R. Stoermer, *ibid.*, 3133; *A.*, i, 785.

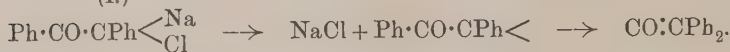
⁴³ G. Schroeter, *ibid.*, 3356; *A.*, i, 773.

⁴⁴ G. Schroeter, *ibid.*, 2336; *A.*, i, 617; H. Wieland, *ibid.*, 4207; *A.*, i, 923.

⁴⁵ G. Schroeter and C. Caspar, *ibid.*, 2336; *A.*, i, 617.

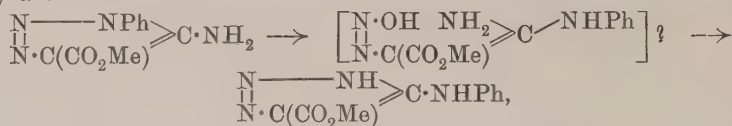


(I.)



(II.)

Numerous instances of the conversion of azimido-compounds into tetrazole or triazole, or of tetrazole into triazole, derivatives have been recorded.⁴⁶ As in these and similar cases the migratory group is held by the remainder of the molecule at two different points, it is impossible to decide the category to which they belong. The instance where phenyl appears to migrate in a triazole ring is admittedly analogous to the reversible decomposition and reproduction of diazoamino-compounds,⁴⁷ and may possibly be represented by a scheme such as:



in which case the migration of the phenyl group would be more apparent than real.

The second class of isomeric changes, namely, those in which the migratory atom or group may easily be removed in some form from the remainder of the molecule under conditions similar to those obtaining during the transformation, includes the cases of desmotropic change, as in keto-enolic conversion, isomeric change in sulphonic acids, and numerous instances of migration of an atom or group from a position outside a benzene nucleus to a point in the nucleus itself. In such cases the labile isomeride has often been regarded as an intermediate product in the sense that the nuclear-substituted form arises by an intramolecular or quasi-intramolecular transformation of the first, although the possibility remained that the stable substance was produced by a separate substitution process, in which the agents were continuously supplied by the decomposition of the labile isomeride. A recent paper marks an epoch in the development of these extremely difficult inquiries. As the result of a long series of experiments, a conclusive decision has been given against intramolecular theories of the migration of halogen in substituted acylanilides:



⁴⁶ M. O. Forster, *Trans.*, 1909, **95**, 184; R. Stollé, *J. pr. Chem.*, 1908, [ii], 78, 544; *Ber.*, 1909, **42**, 1047; *A.*, i, 123, 337; H. von Pechmann and W. Bauer, *Ber.*, 1909, **42**, 659; *A.*, i, 270.

⁴⁷ O. Dimroth, *Annalen*, 1909, **364**, 183; *A.*, i, 267.

Armstrong's view that hydrogen chloride is the active catalyst is confirmed, but this substance acts in virtue of the fact that in its presence an equilibrium is set up, in which free chlorine is produced:



The free chlorine attacks the anilide reversibly at the $\cdot NH \cdot$ group, and irreversibly in the nucleus, so that finally the nuclear-substitution product alone remains. The quantitative evidence, although decisive, is too complicated to give in detail.⁴⁸

It is desirable to avoid the temptation to generalise from this one case, and such attempts must now be worse than useless. It does not follow, for example, that the change of hydrazobenzene into benzidine or of methylaniline into toluidine, etc., are not due to true intramolecular migrations, so that each case must be decided by sound experimental treatment, and a model is not far to seek.

Amongst other isomeric rearrangements, the remarkable migration of acyl groups in derivatives of phenols containing amino- or imino-groups is of great intrinsic importance, and derives additional interest from the part it has played in the controversy respecting the constitution of hydroxyazo-compounds and quinonehydrazones. The conditions under which the migration takes place have been studied by Auwers,⁴⁹ whose conclusions are based on a large mass of experimental material. The spontaneous migration of acyl from oxygen to nitrogen always occurs when the nitrogen is in the α -, β -, or γ -position in an ortho-side-chain, provided that the nitrogen atom is sufficiently basic. A reduction in the negative character of the acyl group hinders the migration, but does not completely inhibit it. Benzoyl wanders less readily than acetyl, the difference being particularly marked in hydrazines when the α -position is blocked, so that migration, if occurring at all, must be to the β -nitrogen atom. When the α -position is already occupied by an acyl group, the migrating group, if the heavier of the two, may displace the other. Thus acetyl is not only displaced from its position in $R \begin{smallmatrix} \text{CH}_2 \cdot NAc \cdot NHPh \\ \text{OX} \end{smallmatrix}$ when X is benzoyl, but also in the presence of an alkali when X is propionyl.

In the simplest case,



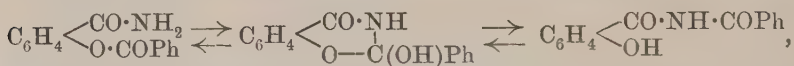
the reaction is not quite instantaneous, and it is occasionally possible to isolate the intermediate O-ester. If *o*-nitro-*p*-tolyl

⁴⁸ K. J. P. Orton and W. J. Jones, *Trans.*, 1909, **95**, 1456; *Proc.*, 1909, **25**, 233.

⁴⁹ K. Auwers, *Ber.*, 1909, **42**, 267; *Annalen*, 1909, **364**, 147; **365**, 278, 291, 314, 343; K. Auwers and F. Eisenlohr, *ibid.*, **369**, 209; *A.*, i, 187, 222, 436, 437, 439, 441, 915.

benzoate is reduced by zinc in acetic acid solution in presence of acetic anhydride, the amino-group is acetylated as fast as it is formed, and the product is the *O*-ester, *o*-acetylamino-*p*-tolyl benzoate. When this is treated with dilute alcoholic soda, the heavier benzoyl group displaces the acetyl, forming *o*-benzoylamino-*p*-cresol. A mere trace of alkali is often sufficient to initiate the isomeric change.

Auwers interprets his results as indicating that the acyl migrates in a free state, a supposition which presents certain difficulties. The fact that the change is confined to ortho-compounds suggests the intermediate formation of a ring, and such an explanation was put forward by McConnan and Titherley in 1906. A further study of reactions of this class confirms this view.⁵⁰ The change of *O*- into *N*-benzoylsalicylamide is reversible, and is readily representable as occurring through the intermediate formation of a hydroxy-metoxazone:



the fact that phenyldihydro-1:3-benzoxazone is converted into *N*-benzoylsalicylamide on oxidation proving the relationship of this ring to the acylated amide. Similar rings may be assumed in all the observed cases. If the rearrangement were due to simple wandering of the free acyl groups, it is difficult to see why it should not occur in many para-compounds.

Isomeric change is often brought about by the influence of light. The change from yellow to red when many phenylhydrazones are exposed to light was attributed by Chattaway⁵¹ to the transformation of the hydrazone into its azo-isomeride, and this conclusion was confirmed and extended by the spectroscopic observations of Baly and Tuck.⁵² The occurrence of such phototropic changes in the hydrazone series is found to be very irregular, the only regularity found among a number examined being that all the β -naphthylhydrazones are phototropic, but none of the α -series.⁵³ The rapidity of change is greatly increased by the presence of a small quantity of a non-phototropic substance, isomorphous with that undergoing the change.⁵⁴ For instance, anisaldehydephenylhydrazone, containing 1 per cent. of anisylidenebenzylamine, is more rapidly and more intensely coloured by light than the pure substance. The decolorisation taking place in the

⁵⁰ A. W. Titherley and W. L. Hicks, *Trans.*, 1909, **95**, 908.

⁵¹ *Trans.*, 1906, **89**, 462.

⁵² *Ibid.*, 982.

⁵³ M. Padoa and F. Graziani, *Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 269; *A.*, i, 964.

⁵⁴ M. Padoa, *ibid.*, i, 694; *A.*, i, 676.

dark is usually accelerated by the presence of an isomorphous admixture.

Salicylidene-*m*-toluidine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, and four other compounds of the same group, are found to change from yellow to orange on exposure to light, the violet rays being the active agency, but no regularity in the exhibition of phototropy in the group has been discovered.⁵⁵ The replacement of the hydroxylic hydrogen by methyl, however, destroys the phototropic properties. The change in darkness is the reverse of that in the light.

The diphenyloctatetrenes⁵⁶ and the stereoisomeric *as*-diphenylethylene, $\text{CPh}_2\cdot\text{CH}_2$,⁵⁷ are other new examples of phototropic substances, the transformation in the latter case being the reverse of that brought about by heating.

Determination of the Constitution of Tautomeric Compounds.

The use of tertiary amines⁵⁸ for distinguishing between acids and pseudo-acids has been applied in two interesting investigations. One of these deals with the structure of hydrogen cyanide, which is found not to yield salts with tertiary amines at 0° , but merely to polymerise, although trialkylammonium cyanides are known to be capable of existence. Primary and secondary amines, however, do yield unstable salts; and it is argued that these bring about a structural change in the hydrogen cyanide, the salts being derived from the tautomeric form. The imidic structure $\text{C}\cdot\text{NH}$ or $\text{C}\vdash\text{NH}$ is deduced from general consideration to be that of the true acid, so that hydrogen cyanide itself is $\text{H}\cdot\text{C}\vdash\text{N}$, or formonitrile.⁵⁹ The communication is a useful contribution to the already somewhat voluminous literature on this subject, and it is satisfactory to note that the results help to strengthen the view which has been adopted by most recent workers on the subject.

A similar investigation on cyanic acid was more difficult, owing doubtless to the greater "affinity" of the acidic form. Most tertiary amines give cyanates with this compound, together with some cyamelide, but tri*iso*amylamine does not give any salt on mixing with the acid at -10° . The tri*iso*amylamine salt, prepared in another way, is found to be quite stable under the conditions employed, and it is therefore concluded that free "cyanic" acid has the pseudo-acid or imido-configuration, $\text{CO}\cdot\text{NH}$, the salts being derived from $\text{CN}\cdot\text{OH}$.

⁵⁵ A. Senier and F. G. Shepheard, *Trans.*, 1909, **95**, 441, 1943.

⁵⁶ H. Stobbe, *Ber.*, 1909, **42**, 565; *A.*, i, 219.

⁵⁷ R. Stoermer, *ibid.*, 4865.

⁵⁸ *Ann. Report*, 1908, 90.

⁵⁹ A. Michael and H. Hibbert, *Annalen*, 1909, **364**, 64; *A.*, i, 91.

Catalytic Actions of Metals and Inorganic Substances.

The methods introduced by Sabatier and Senderens have been extended within the last two years, and catalytic action at high temperatures can now be utilised for preparations which involve processes of reduction, hydration, dehydration, oxidation, and elimination of halogen hydride. There is no reason to doubt that the method is capable of still wider application.

It has been recorded in a previous report⁶⁰ that at 300° alcohol is decomposed by the catalytic action of alumina, yielding ethylene; it has since been observed⁶¹ that at somewhat lower temperatures, namely, between 240° and 260°, and employing an alumina obtained by adding acid to a solution of sodium aluminate, the dehydration process results in the quantitative production of nearly pure ether. A good yield of methyl ether is obtained by the same process at 250—370°, whilst propyl alcohol behaves in a different manner, being mainly converted into an ethylenic hydrocarbon, only 30 per cent. being transformed into dipropyl ether; *isobutyl* alcohol yields *isobutylene* exclusively.

Heated alumina converts acetic anhydride at 300—380° into acetone and carbon dioxide, and if anhydrous thorium dioxide is substituted for alumina, the preparation of ketones from the higher acid anhydrides is readily accomplished. Even with the free acids at 400° it has been found possible to prepare diethyl ketone, dipropyl ketone, and *diisopropyl* ketone. Formaldehyde and carbon dioxide are the products when formic acid is passed over thorium dioxide at 200—250°.⁶²

Senderens has studied the mechanism of the process,⁶³ and concludes that a salt is formed from the acid and the metallic oxide, which is then decomposed.

Although thorium oxide is the most suitable contact material, the oxides of uranium give very good results. It seems essential that the speed of salt-formation and decomposition should not differ very greatly, consequently, very feebly basic oxides, such as those of iron, aluminium, and chromium, or too strongly basic ones, such as those of calcium or zinc, do not give satisfactory results.

Primary aliphatic alcohols may be converted into amines when in contact with ammonia and oxides, such as thorium dioxide or tungsten trioxide, at high temperatures.⁶⁴

⁶⁰ *Ann. Report*, 1908, 77.

⁶¹ J. B. Senderens, *Compt. rend.*, 1909, **148**, 927; *A.*, i, 286.

⁶² J. B. Senderens, *loc. cit.*

⁶³ *Compt. rend.*, 1909, **149**, 213; *A.*, i, 627.

⁶⁴ P. Sabatier and A. Mailhe, *ibid.*, **148**, 898; *A.*, i, 292.

Another novel use of contact reaction, at high temperatures, is in the preparation of aromatic nitro-compounds.⁶⁵ It is found that zinc and copper oxides readily absorb nitrous fumes, and if a mixture of air and the vapour of an aromatic hydrocarbon is passed over the product at 300—350°, nitration takes place. Nitrobenzene, for example, is obtained in quantitative yield by using nitrous fumes produced by electrical methods from the atmosphere, and by combining the process with the reduction method of Sabatier, a method is devised for the direct and continuous production of aniline from benzene.

The employment of nickel oxide with hydrogen under high pressures has been found to be the most efficient means of fully reducing polynuclear hydrocarbons. Fluorene is reduced at 285° and 120 atmospheres to decahydrofluorene, and finally to perhydrofluorene, and acenaphthene yields successively tetra- and decahydroacenaphthene. Retene furnishes first the dodecahydro-derivative, and finally perhydroretene.⁶⁶

An interesting synthesis of ethylene from carbon monoxide and hydrogen has been accomplished at comparatively low temperatures, use being made of reduced nickel distributed on coke at 95—100°; 6 to 8 per cent. of ethylene is obtained, without any trace of formaldehyde. Contrasted with the usual results obtained by the catalytic reduction process, this result is decidedly abnormal, as the formation of methane would be expected. Formaldehyde was also absent when carbon dioxide was reduced, and in this case both ethylene and methane were formed.⁶⁷

Mention was made in last year's report⁶⁸ of the discovery of the powerful reducing effect at the ordinary temperature of hydrogen in presence of palladium hydrosol, and the work has been considerably extended.⁶⁹ In one particular the method has advantages over all other reduction processes, namely, in the preparation of saturated ketones from their $\alpha\beta$ -unsaturated derivatives,⁷⁰ for the latter, when subjected to the action of other reducing agents, usually yield alcohols or pinacones.

Allied to the foregoing method is that recently used for reducing phenanthrene; here hydrogen was led into a boiling ethereal solution of the hydrocarbon in presence of platinum-black, when

⁶⁵ Chemische Fabrik Grünau Landshoff & Meyer Akt.-Ges., D.R.-P. 207170; *A.*, i, 295.

⁶⁶ W. N. Ipatieff, *Ber.*, 1909, **42**, 2092 and 2097; *A.*, i, 466 and 472.

⁶⁷ E. I. Orloff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1588; *A.*, i, 77.

⁶⁸ *Ann. Report*, 1908, 76.

⁶⁹ C. Paal and K. Roth, *Ber.*, 1909, **42**, 1541; C. Paal and J. Gerum, *ibid.* 1553; C. Paal and W. Hartmann, *ibid.*, 545; *A.*, i, 358, 381, 545;]

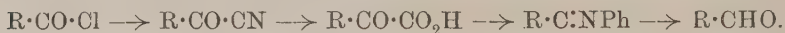
⁷⁰ A. Skita, *ibid.*, 1627; *A.*, i, 479.

in six to eight hours nearly pure 9:10-dihydrophenanthrene was obtained. The reaction also took place at the ordinary temperature, but required some two days to reach completion.⁷¹

Practical Methods and General Reactions.

When carbon dioxide is passed into aqueous solutions of alcohols, simple or polyhydric sugars, or other hydroxy-compounds in presence of lime, soluble calcium double salts of the type $(R \cdot O \cdot CO_2)_2Ca$ are formed. These are unstable, however, and decompose when heated; in solution they are only capable of existing in equilibrium with their generators or dissociation products.⁷²

A useful method of obtaining an aldehyde from the corresponding acid chloride consists in first converting the latter into the acid cyanide by Claisen's method, and then, from the α -carboxylic acid which this furnishes on hydrolysis, the phenylimide of the aldehyde is prepared by boiling with aniline in accordance with Bouveault's directions, and is decomposed by dilute sulphuric acid into aldehyde and aniline⁷³:



The preparation of acraldehyde, hitherto a tedious and disagreeable operation, is much simplified if orthophosphoric acid, with sodium chloride, is used as dehydrating agent. The materials used need not be very dry, large quantities may be employed, and the operation may be conducted on a water-bath.⁷⁴ The use of orthophosphoric acid as a dehydrating catalyst in preparative work is most advantageous, owing to the absence of carbonising effects, but it does not yet seem to have been sufficiently fully investigated, in spite of the striking demonstration of its utility given by Newth some years ago.

When aldehydes are made from most primary alcohols by means of a solution of chromic anhydride on acetic acid, poor yields are obtained, owing to the formation of acetates derived from the enolic forms of the aldehydes: $>C:CH \cdot OAc$. These enolic aldehyde acetates may also be prepared by boiling the aldehydes with acetic anhydride; in this manner, for example, phenylacetaldehyde gives rise to phenylvinyl acetate:



⁷¹ J. Schmidt and E. Fraser, *Ber.*, 1908, **41**, 4225; *A.*, i, 19.

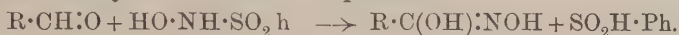
⁷² M. Siegfried and S. Howwjan, *Zeitsch. physiol. Chem.*, 1909, **59**, 376; *A.*, i, 352.

⁷³ F. Mauthner, *Ber.*, 1909, **42**, 188; *A.*, i, 160; compare L. Bouveault, *Compt. rend.*, 1896, **122**, 1543; *A.*, 1896, i, 649.

⁷⁴ G. F. Bergh, *J. pr. Chem.*, 1909, [ii], **79**, 351; *A.*, i, 363.

The acetates are easily oxidised by ozone, so that the discovery provides a novel method for the degradation of aldehydes,⁷⁵ and one instance where important results have been obtained in applying it is dealt with in the section on the terpenes.

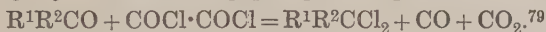
Aldehydes form hydroxamic acids with benzenesulphohydroxamic acid and sodium hydroxide, and this forms a good distinction between aldehydes and other compounds:



It is interesting that γ -hydroxyaldehydes, such as erythrose or arabinose, do not respond, owing to the engagement of the carbonyl group in ring formation, and as γ - and δ -hydroxy-, -keto-, and -amino-aldehydes give negative results too, a similar ring structure may be present in these; hydroxymethylene compounds, also, give negative results.⁷⁶

Sulphur monochloride, S_2Cl_2 , acts on the sodium salts of carboxylic acids suspended in petroleum, and appears to yield compounds in which S_2 replaces the hydrogen of two molecules of the acid; for example, sodium benzoate yields a compound which is probably $(\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{S})_2$. These compounds decompose readily, and sometimes spontaneously, the products being sulphur, sulphur dioxide, and the acid anhydride.⁷⁷

Oxalyl chloride proves to be an interesting synthetic reagent, resembling carbonyl chloride in many of its reactions. Thus, it condenses with dimethylaniline to form *p*-tetramethyldiaminobenzil, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$.⁷⁸ In other cases it behaves as a chlorinating agent, resembling phosphorus pentachloride:



Alkyl chlorocarbonates are found to be convenient alkylating agents in a number of cases. The mixed carbonic esters of phenols lose carbon dioxide on heating, and pass into alkyl ethers of phenols: $\text{Ar}\cdot\text{O}\cdot\text{CO}\cdot\text{OR} = \text{CO}_2 + \text{Ar}\cdot\text{O}\cdot\text{R}$. This is a general reaction, although not always taking place with equal readiness.⁸⁰ The same reagents may be employed to esterify carboxylic acids, the mixed anhydrides, $\text{R}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{R}^1$, formed at first decomposing spontaneously.⁸¹

The use of derivatives for the protection of hydroxyl groups

⁷⁵ F. W. Semmler, *Ber.*, 1909, **42**, 584, 1161; *A.*, i, 289, 364.

⁷⁶ A. Angeli and G. Marchetti, *Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 360; *A.*, i, 12.

⁷⁷ W. S. Denham, *Trans.*, 1909, **95**, 1235.

⁷⁸ H. Staudinger and H. Stockmann, *Ber.*, 1909, **42**, 3485; *A.*, i, 796.

⁷⁹ H. Staudinger, *ibid.*, 3966; *A.*, i, 905.

⁸⁰ A. Einhorn, *ibid.*, 2237, 2772; *A.*, i, 568, 645.

⁸¹ J. Herzog, *ibid.*, 2557; *A.*, i, 568.

during the condensation of acids to form polypeptides was introduced by Fischer, and has found numerous applications. The condensation of methyl chlorocarbonate with salicylic acid does not take place under the usual conditions, but is readily accomplished in presence of dimethylaniline.⁸²

A new series of oxidising agents, which may prove valuable on account of the smoothness with which they react, consists of the nitrates of aldehydes and ketones.⁸³ Anthracene, for example, may be dissolved in benzaldehyde nitrate by gently warming, and pure anthraquinone crystallises on cooling. Borneol is oxidised to camphor.

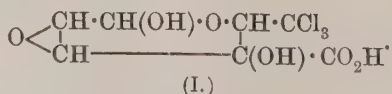
True nitroso-compounds, containing the group $\text{:CH}\cdot\text{NO}$, are usually difficult to obtain, owing to the ease with which this structure undergoes change into the isomeric oxime group, $\text{:C}\cdot\text{N}\cdot\text{OH}$. A simple and general method for the preparation of α -nitroso-esters consists in passing nitrous fumes from nitric acid and arsenious anhydride into β -ketonic esters at 0° :



The esters are blue liquids, often unstable to light, and are rapidly changed by water or alkalis, the colour disappearing owing to conversion into oximino-compounds, or, in part, to polymerisation. With Caro's reagent or hydrogen peroxide, they are converted into the corresponding nitro-esters.⁸⁴

Carbohydrates and their Allies.

The aldehydoses and aldehydoses may be divided into four groups, according to the configuration of the three carbon atoms which are adjacent to the terminal $\cdot\text{CHO}$ group, and it is possible to ascertain in a simple manner the class to which any particular sugar must be referred. The sugar is condensed with chloral, and the product, its "chloralose," is examined; if this is found identical with one of those already known, the class to which the aldose belongs is decided. If not, the chloralose is oxidised; chloralic acids (I) are obtained—substances which contain only five of the original carbon atoms of the sugar, the terminal carbon atoms of the hexose molecule remote from the $\cdot\text{CHO}$ group having disappeared:



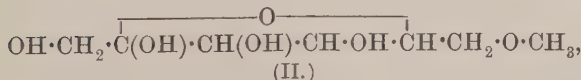
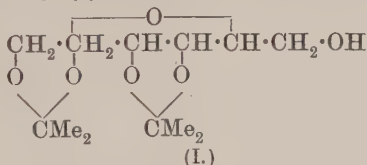
⁸² E. Fischer, *Ber.*, 1909, **42**, 215; *A.*, i, 161.

⁸³ A. A. Shukoff, D.R.-P. 206695; *A.*, i, 238.

⁸⁴ J. Schmidt and K. T. Widmann, *Ber.*, 1909, **42**, 497, 1886; *A.*, i, 134, 453.

Four isomerides are theoretically capable of existence, corresponding with the four above groups of aldoses, and the identity of the products from any sugar determines the series to which it belongs. All the isomerides have been described except that corresponding with talose and ribose. As an instance of the manner in which the method may be applied, it may be stated that arabinose yields two such chloralic acids, and one of these is identical with one of the pair which is furnished by galactose; a similar partial identity is observed in the acids obtained respectively from xylose and dextrose.⁸⁵

A suggestive method, probably capable of wide application, for attacking the certain questions arising in the study of sugar derivatives depends on the principle that methylation of the free hydroxyl groups protects these from attack during subsequent operations. Thus the constitution of the condensation product of lævulose with acetone has been shown, with some degree of certainty, to be represented by (I):



and (II) is the most probable structure for the monomethyl lævulose obtained from it by hydrolysis, the evidence being that the latter substance yields, on mild oxidation, an acid which has the composition of dihydroxydimethoxybutyric acid, but is incapable of forming a lactone.⁸⁶

It is interesting that α -monomethyl lævulose gives a positive result with the Tollens test, which was supposed to be applicable only to pentoses.

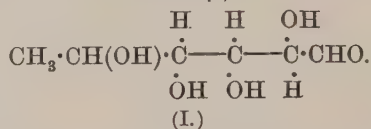
Biologically the synthesis of sugars from formaldehyde is a reversible process, but hitherto the question of the artificial production of formaldehydes from a sugar by a simple chemical process at the ordinary temperature has not been closely investigated. The electrolysis of dextrose solutions in dilute sulphuric acid leads to a change, which is the inverse of the type of the usual synthetic process: $\cdot\text{CH}(\text{OH}) \cdot \text{CH}:\text{O} = \cdot\text{CH}:\text{O} + \text{CH}_2:\text{O}$, and formaldehyde, *d*-arabinose, and oxidation products are found in the resulting

⁸⁵ M. Hanriot, *Compt. rend.*, 1909, **148**, 487, 640; *A.*, i, 206, 287.

⁸⁶ J. C. Irvine and A. Hynd, *Trans.*, 1909, **95**, 1220.

solutions. In association with the fact that pure glycerose has been observed to yield a pentose when condensed, pointing to depolymerisation of the glycerose in the above sense, the observation is a very significant one, and suggests new lines of attack on the problems relating to the manner in which the organism attacks its foods in building new molecular complexes.⁸⁷

Definite light has been thrown on the configuration of fucose by oxidising it with dilute nitric acid, when a trihydroxyglutaric acid is obtained, which is the optical antipode of that which rhamnose with known constitution yields in similar circumstances. The configuration of fucose⁸⁸ is therefore (I):



A novel synthetic method for the preparation of disaccharides has proved successful in at least one instance, and promises to be of great importance. A substance of the type of trehalose is the first to be prepared by this process, which consists in shaking β -aceto-dextrose in moist ether with silver carbonate, or by agitating a solution of the tetracetylaldose with phosphoric oxide. The resulting octa-acetyldisaccharide is easily hydrolysed by baryta water, yielding the new sugar, in this case *isotrehalose*, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which does not reduce Fehling's solution, and yields dextrose on hydrolysis with acids.⁸⁹

Investigations on the physical properties of the carbohydrates of high molecular weight have led to numerous striking observations, and among the most interesting of these is the discovery that the molecular volume of soluble starch is only about nine-tenths of that calculated on Traube's data for the formula $\text{C}_6\text{H}_{10}\text{O}_5$, although the observed value for solid anhydrous starch, on the other hand, is nearly the normal one. The suggestion is advanced by Cross and Bevan,⁹⁰ and supported by M. Traube, that the anomalous value for soluble starch is to be accounted for by the occurrence of ring formation.

Recent investigations on the composition of the products termed "cellulose hydrates," including mercerised cellulose, indicate that when freed from all traces of hygroscopic moisture, these substances have the same composition as ordinary cellulose, namely, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$;

⁸⁷ W. Löb, *Biochem. Zeitsch.*, 1909, **17**, 182, 343, 516; *A.*, i, 352, 456, 767; compare also *Ann. Report*, 1908, 88.

⁸⁸ B. Tollens and F. Rorive, *Ber.*, 1909, **42**, 2009; *A.*, i, 555.

⁸⁹ E. Fischer and K. Delbrück, *ibid.*, 3776; *A.*, i, 533.

⁹⁰ C. F. Cross and E. J. Bevan, *ibid.*, 2198, 2204; *A.*, i, 555.

those termed "hydrocelluloses," on the other hand, appear to contain chemically combined water, and in this sense are true cellulose hydrates, analogous in composition to the more complex products of starch hydrolysis.⁹¹

Before concluding this chapter, attention may be drawn to experiments showing that " β -hydroxy- δ -methylfurfuraldehyde" is formed by the dry distillation of hexoses or on heating these compounds with dilute acids,⁹² ketoses yielding a larger proportion than aldoses. The substance has often been mistaken for furfuraldehyde, and it plays an important part in certain well-known tests. The observations recall Fenton's work on bromomethylfurfuraldehyde, to which the hydroxyaldehyde is closely related, and the most recent evidence tends to show that the hydroxyl group in the latter replaces a hydrogen atom in the methyl group, and not one in the ring,⁹³ as is usually assumed.

Ketens.

Researches in the keten series have not been very numerous. The conditions of formation of keten from α -halogenated acetyl halides have been investigated,⁹⁴ and a comparison of the products of polymerisation of ketens has led to the conclusion⁹⁵ that the bimolecular compound described⁹⁶ as acetylketen, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}$, is really a cyclic compound, $\text{O}\cdot\text{C}\begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix}\text{C}\cdot\text{OH}$, its chemical inertness being opposed to the open-chain formula.

Ethyl ethylketencarboxylate, $\text{CO}_2\text{Et}\begin{smallmatrix} \text{Et} \end{smallmatrix}\text{C}\cdot\text{CO}$, differs greatly from the other disubstituted ketens, being colourless and incapable of forming additive compounds.⁹⁷ It readily polymerises to form a cyclobutane derivative, and in its properties resembles rather the aldo-ketens, with only one substituting group, than the keto-ketens. In the action of fatty triamines on isobutyryl chloride, dimethylketen is first formed, polymerising immediately to 1:3-diketotetramethylcyclobutane, $\text{CMe}_2\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\text{CMe}_2$, and an additive compound, $\text{CMe}_2\cdot\text{CO}\cdot\text{N}\text{Et}_3$, is formed at the same time.⁹⁸ Several

⁹¹ H. Ost and F. Westhoff, *Chem. Zeit.*, 1909, **33**, 197; *A.*, i, 210.

⁹² W. Alberda van Ekenstein and J. J. Blanksma, *Chem. Weekblad*, 1909, **6**, 217; *A.*, i, 288.

⁹³ H. J. H. Fenton and F. Robinson, *Trans.*, 1909, **95**, 1334.

⁹⁴ H. Staudinger and J. Kubinsky, *Ber.*, 1909, **42**, 4213; *A.*, i, 880.

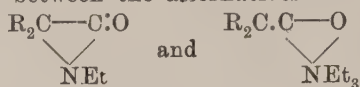
⁹⁵ H. Staudinger and S. Bereza, *Ber.*, 1909, **42**, 4908.

⁹⁶ *Ann. Report*, 1908, 84.

⁹⁷ Staudinger and Bereza, *loc. cit.*

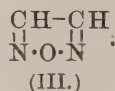
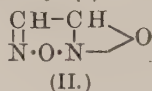
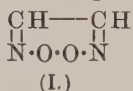
⁹⁸ E. Wedekind and M. Miller, *Ber.*, 1909, **42**, 1269; *A.*, i, 459.

compounds of similar composition have been obtained, and have been found to have very great stability, entirely unlike the previously known keten bases, which have all the characters of mere additive products. The reactions of the new "ketenium" compounds point rather to a cyclic structure, it being impossible to decide at present between the alternatives:



Furoxans, Vitriole Oxides, and Fulminic Acid.

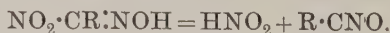
Among the heterocyclic rings which contain nitrogen directly attached to oxygen, and are thus derived from hydroxylamine or dihydroxylamine, the so-called "glyoxime peroxides" are at present evoking much interest. According to Wieland and his co-workers,⁹⁹ these are in reality derivatives of furoxan (II), which is an oxide of furazan (III), the structure previously attributed to "glyoxime peroxide" being represented by (I):



Furoxans may be formed by polymerisation of nitrile oxides, to which Wieland attributes the general formula $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{R} \cdot \text{C}=\text{N} \end{array}$.¹ The first representative of this series, benzonitrile oxide, was originally obtained by Werner on removing the elements of hydrogen chloride from benzhydroximic chloride:



A more general reaction for preparing these substances in a termolecular form is offered by the mode of spontaneous decomposition in solution of the alkali salts of the nitrolic acids:

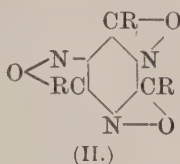
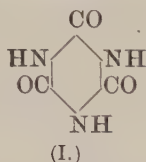


In this manner, termolecular oxides of formonitrile, acetonitrile, and benzonitrile are formed readily enough. Their reactions closely resemble those of benzonitrile oxide itself, and they are prone to undergo transformations which recall the well-known Hofmann change which bromoamides undergo in presence of alkali; thus the phenyl derivative in hot xylene is quantitatively converted into phenylcarbimide: $(\text{Ph} \cdot \text{CNO})_3 = 3\text{Ph} \cdot \text{N} : \text{C} : \text{O}$.

⁹⁹ H. Wieland and L. Semper, *Annalen*, 1907, **358**, 36; H. Wieland and A. Gmelin, *Ber.*, 1908, **41**, 3512; *ibid.*, 1909, **367**, 52 and 80; *A.*, 1908, i, 108, 1013; 1909, i, 609 and 610; *Ann. Report*, 1907, 161.

¹ Compare *Ann. Report*, 1907, 138.

Analogies are drawn between cyanuric acid (I) and the trimolecular nitrile oxides, for which the formula (II) is suggested:



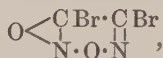
There is a close relationship between the nitrile oxides and fulminic acid, on the one hand, and furoxans (or "glyoxime peroxides") on the other. Benzonitrile oxide, when formed by the spontaneous decomposition of benzylnitrolic acid, polymerises to diphenylfuroxan:



but methylnitrolic acid, in similar circumstances, gives rise to fulminic acid:

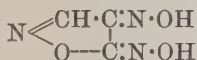


A further connexion between fulminic acid and the furoxans has been elicited by a recent investigation of the substance which Kekulé obtained from bromine and mercury fulminate. This substance, long known as "dibromonitroacetonitrile," appears in reality to be dibromofuroxan:



which is attested by the ease with which it yields oximino-derivatives of oxamide with ammonia and organic bases.²

Fulminic acid is found to be soluble in ether, and also to be volatile in the vapour of that liquid at low temperatures. Metafulminuric (isocyanuric) acid is the sole product of its spontaneous polymerisation, and for this polymeride the formula



is adopted as the most satisfactory one in view of the most recent evidence.³

² H. Wieland, *Ber.*, 1909, **42**, 803, 816, 820, 4199; H. Wieland and H. Hess, *ibid.*, 4175, 4199; *A.*, i, 215, 216, 217, 882, 884.

³ H. Wieland and H. Hess, *ibid.*, **43**, 1346; *A.*, ii, 369.

Proteins, Polypeptides, and Amino-acids.

In this section of organic chemistry the progress is very steady, and there are signs that before long the intricacy of this subject may challenge comparison with that of colouring matters. The recognition of the component groups and their mode of attachment in natural materials probably occupies first place in the estimation of chemists, and whether the methods are analytic or synthetic is of small consequence provided that they are trustworthy. Abderhalden's work on the proteins has already attracted much attention, and among his interesting communications during the year, one on the products of partial hydrolysis of certain proteins is unusually suggestive, although not altogether novel in principle.⁴ He proposes to undertake systematic researches on the products of the partial hydrolysis of complicated proteins, and to separate and examine the intermediate products, with a view to ascertaining what is the structure of each. In other words, he intends to examine the structure of each by finding the way in which the ultimate residues are linked in pairs or trios.

He has already made preliminary examinations of several complicated proteins in this manner, including edestin. This furnishes three polypeptides, of which one contained the residues of glutamic acid and tryptophan, another those of glutamic acid, tryptophan, and leucine, and the last those of tyrosine, glycine, and leucine. In this connexion Mathieu suggests measuring the speed of hydrolysis of proteins by acids. With gelatin, "breaks" are found in the curve obtained, which are considered to indicate successive stages in the hydrolysis. Numerous communications on the composition and cleavage products of natural proteins by acids have appeared, and the use of hydrofluoric acid in this connexion is being carefully examined.⁵ The dilute acid yields, according to the conditions imposed, varying proportions of diamines and amorphous polypeptides; the latter in certain instances give crystalline picrates. The method has been applied to pepsin extract and gelatin with definite results, and as the acid does not give rise to condensation of the simpler molecules, it is concluded that the products of partial hydrolysis represent pre-existing natural complexes. Important development along these lines may be expected in the near future.

The action of cold alkalis on the proteins has also given some interesting results. It is found that certain protamines undergo a

⁴ E. Abderhalden, *Zeitsch. physiol. Chem.*, 1909, **58**, 373, and **62**, 315; *A.*, i, 273, 859.

⁵ L. Hugounenq and A. Morel, *Compt. rend.*, 1909, **148**, 236, and **149**, 41; *A.*, i, 195, 685.

diminution in rotatory powers, probably in the main a result of racemisation, although hydrolysis can be detected when the action of the alkali is prolonged at higher temperatures.⁶

A novel method for isolating the monoamino-acids obtained in the hydrolysis of the proteins has been suggested, depending on the fact that their betaines, unlike those of the diamines or polypeptides, are easily prepared by methylation and form characteristic aurichlorides which are very easily isolated.⁷

The synthetic production of polypeptides is being pushed on with undiminished vigour, but only a short reference to some of the results can be given here.

Starting with the products obtained by the action of phosphorus pentachloride on benzoylpiperidine, Braun has succeeded in effecting a new synthesis of inactive lysine.⁸ By similar methods, E. Fischer and G. Zemplén have synthesised ornithuric acid (dibenzoyl- $\alpha\delta$ -diaminovaleric acid) and proline⁹ from piperidine, and these authors have also resolved proline into its optically active isomerides.

A variety of synthetic polypeptides with *l*-leucine, α -alanine, glycine, *l*-cystine, glutamic acid, and other residues have been described.¹⁰

An interesting group of natural vegetable acids, for which the name "etholides" is proposed, is found in certain Coniferae. The members resemble the polypeptides in their structure, but the units are linked by oxygen instead of nitrogen. They are, in other words, systems of condensed hydroxy-acids, and their general structure may be represented as:

$R \cdot CH(OH) \cdot [CH_2]_n \cdot CO \cdot O \cdot CHR' \cdot [CH_2]_m \cdot CO \cdot O \cdot CHR'' \cdot [CH_2]_p \dots CO_2H$,
when R, R', R'', etc., and n, m, p, etc., may or may not be identical.¹¹

Putrefaction of Amino-acids.

It will be remembered that amino-acids are converted by yeasts into the next lower alcohols with loss of ammonia and carbon dioxide. During the putrefaction of such compounds, on the other hand, the amino-group may be replaced by hydrogen instead of by hydroxyl, with or without loss of the carboxyl group. Aspartic acid first loses its amino-group and gives succinic acid, which

⁶ A. Kossel and F. Weiss, *Zeitsch. physiol. Chem.*, 1909, **59**, 492; **60**, 311; *A.*, i, 542.

⁷ R. Engeland, *Ber.*, 1909, **42**, 2962; *A.*, i, 856.

⁸ J. von Braun, *ibid.*, 839; *A.*, i, 229.

⁹ *Ber.*, 1909, **42**, 1022; *A.*, i, 303.

¹⁰ E. Fischer and J. Steingroever, *Annalen*, 1909, **365**, 167; E. Fischer and O. Gerngross, *Ber.*, 1909, **42**, 1485; *A.*, i, 366 and 367, etc.

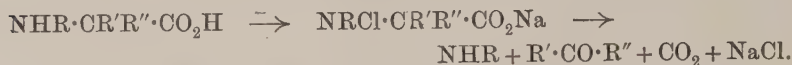
¹¹ J. Bougault and L. Bourdier, *Compt. rend.*, 1908, **147**, 1311; *A.*, i, 82.

afterwards furnishes carbon dioxide and propionic acid; glutamic acid is converted into butyric acid.¹²

Similarly, tyrosine gives rise to *p*-hydroxyphenylethylamine.¹³

α -Amino-acids, containing primary or secondary amino-groups, yield chloroamino-derivatives with solutions of hypochlorites, which at 40–50° are converted into the aliphatic aldehydes, or aldehydes with one carbon atom less than the original amino-acid.¹⁴

The other products are ammonia or a primary amine and carbon dioxide:



This discovery promises not only to furnish a novel method for obtaining ketones and aldehydes from natural amino-acids, but may also prove to be of considerable value in determining the constitution of new amino-acids and in discriminating between these and various polypeptides.

Hydroaromatic Compounds.

Recent controversies on the terpinenes and on substituted dihydrobenzenes illustrate the very considerable difficulties which beset the path of the experimenter in this field, and it is evident that hydroaromatic compounds are exceptionally labile, so that evidence as to constitution must be based on methods which admit of no possibility of structural change; moreover, generalisations are equally dangerous. A compound to which the constitution 1:1-dimethyl- $\Delta^{2:5}$ -cyclohexadiene was ascribed by Harries and Antoni¹⁵ on apparently quite reasonable grounds, has recently been shown to be a mixture of 1:2- and 1:3-dimethylcyclohexadienes.¹⁶

Previous results had suggested that when either of the methyl groups of the complex :CMe_2 migrate, they are afterwards found attached to adjacent carbon atoms, but the appearance of the 1:3-dimethyl derivative in the above mixture shows that the rule is not an infallible one.

The behaviour of benzene derivatives when subject to the action of reducing agents is capricious. Thus, *m*-hydroxybenzoic acids yield the hexahydro-derivatives quite readily with sodium and amyl alcohol, but those acids which contain the hydroxyl and carbonyl groups in the para-position are not appreciably changed under these

¹² L. Borchardt, *Zeitsch. physiol. Chem.*, 1909, **59**, 96; *A.*, i, 210.

¹³ G. Barger, *ibid.*, 1908, **61**, 188; *A.*, i, 701.

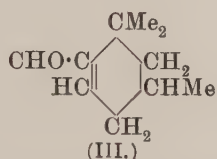
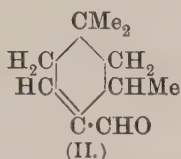
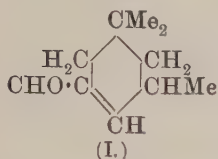
¹⁴ K. Langheld, *Ber.*, 1909, **42**, 392, 2360; *A.*, i, 138, 557.

¹⁵ *Annalen*, 1903, **328**, 88; *A.*, 1903, i, 613.

¹⁶ A. W. Crossley and Miss N. Renouf, *Trans.*, 1909, **95**, 930.

conditions,¹⁷ and the explanation of this is not yet forthcoming. The *o*-hydroxybenzoic acids, as is well known, are converted by ring fission into derivatives of adipic acid.

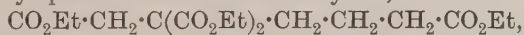
The odour of violets, which is associated with certain aldehydes containing the group :C:C·CHO, has been the subject of a lengthy series of investigations. Various aldehydes were prepared, including the following:



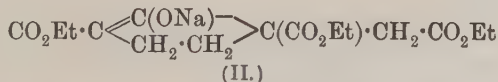
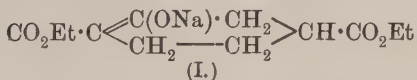
From the results it is concluded that for an aldehyde to possess the perfume of violets (*a*) it must contain the *cyclogeraniolene* ring, (*b*) the aldehyde group must be in the ortho-position with reference to a methyl group or a dimethyl group, and if it lies between them, and therefore is ortho to both, the odour is intense.¹⁸

The relative stabilities of saturated carbon rings are in fair accordance with the requirements of Baeyer's strain theory, although it does not supply a full explanation of all the facts. Recent observations tend, on the whole, to strengthen the view that the saturated pentamethylane ring is the most stable one. The case of unsaturated rings is not so simple, and at present no general rule can be drawn.

When ethyl pentane- $\alpha\delta\delta\epsilon$ -tetracarboxylate,



reacts with sodium, it furnishes a *cyclohexane* derivative (I), although it might equally well have yielded a *cyclopentane* derivative (II).¹⁹



Again, in the cyclic condensation of diketones, it appears that the unsaturated five-carbon ring is most easily produced, the six-carbon

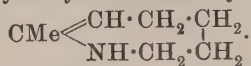
¹⁷ O. Baudisch, G. S. Hibbert, and W. H. Perkin, jun., *Trans.*, 1909, **95**, 1870; O. Baudisch and W. H. Perkin, jun., *ibid.*, 1883; A. N. Meldrum and W. H. Perkin, jun., *ibid.*, 1889.

¹⁸ G. Merling, R. Welde, H. Eichwede, and A. Skita, *Annalen*, 1909, **366**, 119; *A.*, **i**, 479.

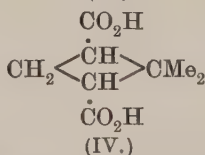
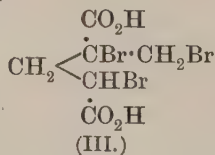
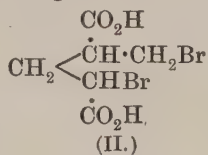
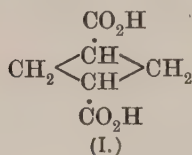
¹⁹ Miss M. E. Dobson, J. Ferns, and W. H. Perkin, jun., *Trans.*, 1909, **95**, 2010.

ring with difficulty, whilst the formation of a seven-carbon ring has not yet been observed.²⁰

Seven-membered rings, containing an atom of nitrogen, appear to be formed with some ease. For example, methyl ϵ -aminoamyl ketone picrate, when merely heated at 100°, is converted into the picrate of *cyclo*-2-methyldehydrohexamethyleneimine²¹:

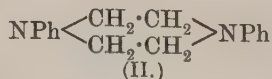
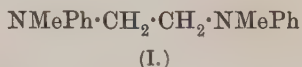


Cyclic compounds show striking irregularities. *cyclo*Butanedicarboxylic acid (I) is attacked by fuming hydrobromic acid at 100°, giving the open-chain compound (II). Further, if (I) is brominated, it yields the bromo-derivative (III), and this is quantitatively converted by zinc and acetic acid into the original *cyclo*-butanedicarboxylic acid (I). On the other hand, the *gem*-dimethyl derivative of (I), namely, norpinic acid (IV), is quite stable²² under conditions which lead to ring scission with (I):



A similar change in stability, but in the opposite sense, is noticed in nopinol, the six-carbon ring in which is rendered more stable by the replacement of hydrogen by methyl.²³

Two interesting cases of the elimination of an alkyl group from a dialkylated aniline owing to ring formation were described almost simultaneously.²⁴ Thus, when ethylaniline and ethylene dibromide react in the proportions 4 : 1, the products are diphenyldimethylethylenediamine (I) and ethylaniline hydrobromide; when the proportions are 2 : 1, diphenylpiperazine (II) and diethylamine hydrobromide are formed:



²⁰ E. E. Blaise and A. Koehler, *Compt. rend.*, 1909, **148**, 852; *A.*, i, 287.

²¹ S. Gabriel, *Ber.*, 1909, **42**, 1249; *A.*, i, 492.

²² W. H. Perkin, jun., and J. L. Simonsen, *Trans.*, 1909, **95**, 1166.

²³ Wallach, *Annalen*, 1907, **356**, 241; *A.*, 1907, i, 936.

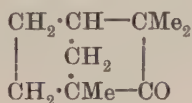
²⁴ H. R. Le Sueur, *Trans.*, 1909, **95**, 273; J. C. M. Dunlop and H. O. Jones, *ibid.*, 416.

The interaction of ethylaniline and $\alpha\alpha'$ -dibromoadipic acid also leads to the formation of a ring compound and diethylaniline hydrochloride.

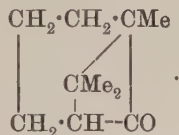
Terpenes and Allied Compounds.

The output of papers on this section of organic chemistry has not been appreciably less than usual, and much of it has contained matter of fundamental importance. It will not be possible to deal with more than a small proportion of these, and recent work on the constitution of camphor derivatives, terpinenes, etc., must inevitably be left for inclusion in subsequent reports. General interest this year has been arrested mainly by the progress in the chemistry of fenchone, pinene, and camphene.

Fenchone.—A definite step towards agreement on the subject of the constitution of this ketone has been taken, Wallach's formula being abandoned by its proposer as incompatible with the results of his most recent researches.²⁵ Two others have been proposed, namely, (I) by Semmler, and (II) by Glover:



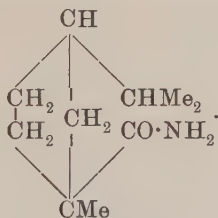
(I.)



(II.)

The former is, for various reasons, the one which finds most general favour, and readily accounts for the formation of dehydrofencholenic acid, but Wallach is not yet prepared to accept it without reserve.

Last year Bouveault and Levallois were able²⁶ definitely to establish the formula for dihydrofencholenamide (fencholamide) (II), the substance into which fenchone is converted by sodamide:

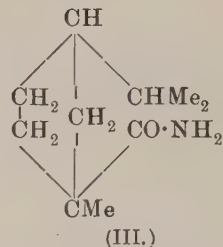
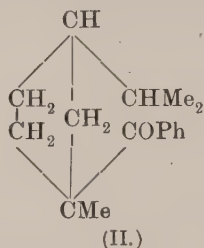
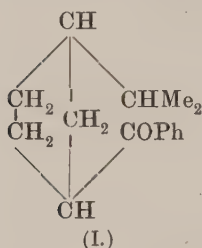


The complete synthesis of this compound, for which Wallach proposes the term fencholamide, as it is the analogue of campholamide in the fenchone series, has now been accomplished, dihydrocampholenic acid (compare section on camphene) being an

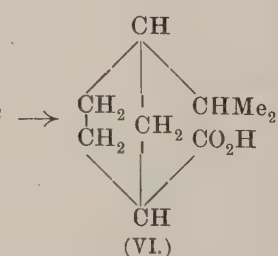
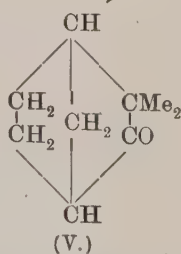
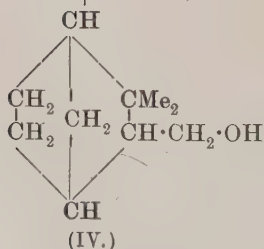
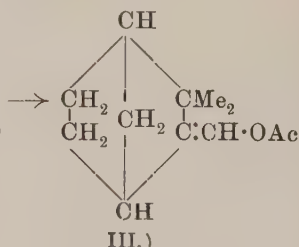
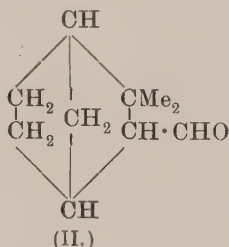
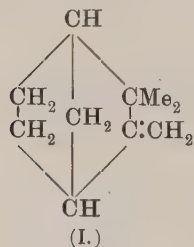
²⁵ O. Wallach, *Annalen*, 1909, **369**, 63; *A.*, i, 811.

²⁶ *Compt. rend.*, 1908, **146**, 180; *A.*, i, 1908, 193.

intermediate step. This acid was converted into its chloride, and the product, by the Friedel-Crafts reaction, into its phenyl ketone (I), from which a sodium derivative is obtained by the action of sodamide. The sodium atom is readily exchanged for methyl, and the resulting ketone (II) undergoes the normal decomposition with sodamide which leads to the production of benzene and dihydrofencholenamide (fencholamide)²⁷ (III):



Camphene.—Consideration of Semmler's recent researches on this interesting hydrocarbon or mixture of hydrocarbons, combined with the synthetic work of Bouveault and his collaborators, make it appear probable that the stage preceding a general agreement on the question of its exact nature has been reached.

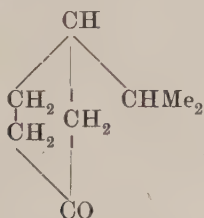


²⁷ L. Bouveault and G. Blanc, *Compt. rend.*, 1909, **148**, 1524; compare also L. Bouveault and Levallois, *ibid.*, 1899; *A.*, **i**, 497, 595.

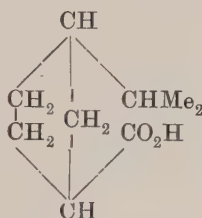
Étard's camphenilaldehyde (II) yields an *enol*-acetate, and this can be reduced to camphenyl alcohol, from the chloride of which, on treatment with sodium and alcohol, camphene (I), mixed with a little *isocamphene*, is regenerated. Thus, the central nuclei and the mode of attachment of the side groups are proved to be identical in camphene and camphenilaldehyde.

Wagner's camphenilone (V) is produced by the action of moist ozone on either camphene or *enol*camphenilaldehyde acetate (III), and there is no reason to suppose that this most trustworthy oxidation method can lead to those bewildering structure changes so frequent in the terpene series²⁸; the weak link in the chain of evidence is probably the next one (where the degradation process is more violent and probably less trustworthy from this point of view than those used elsewhere, and, furthermore, the step has not yet been retraced). On heating camphenilone with sodamide, it is converted into the amide of dihydrocampholenic acid (VI), the total synthesis of which has been accomplished in the following manner.

Starting from β -isopropyladipic anhydride, this was converted by heating into 3-isopropylcyclopentanone (VII), which was identified with a ketone obtained from camphenilone. By reduction, the corresponding alcohol was obtained. The corresponding bromo-derivative in ether reacted with magnesium and carbon dioxide, yielding finally a carboxylic acid (VIII), the amide of which proved to be identical with that obtained directly from camphenilone²⁹:



(VII.)



(VIII.)

Pinene.—The syntheses from nopinone of β -pinene and fenchene through nopinolacetic acid were recorded in the previous report. O. Wallach has now succeeded³⁰ in isolating synthetic *laevorotatory* α -pinene from the products of the destructive distillation of this acid in a current of hydrogen, proving its identity by showing that it furnishes *l*-pinonic acid on oxidation.

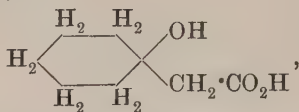
In connexion with synthetic terpenes, an important paper has

²⁸ F. W. Semmler, *Ber.*, 1909, **42**, 246, 962; *A.*, i, 170, 312

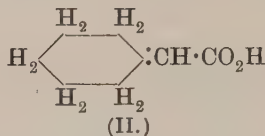
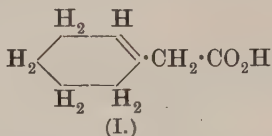
²⁹ L. Bouveault and G. Blanc, *Compt. rend.*, 1908, **147**, 1314; *A.*, i, 108.

³ *Annalen*, 1909, **368**, 1; *A.*, i, 726.

appeared, giving generalisations of the results obtained with cyclic hydroxy-acids during the past few years.³¹ It is found that the hydroxy-acids of the type



obtained by the action of zinc and ethyl bromoacetate on cyclic ketones, are dehydrated in either or both of two ways, yielding the product (I) or (II), the course of the reaction depending on the structure of the acid as well as on the nature of the dehydrating agent:



Usually potassium hydrogen sulphate or phosphoric oxide favours the formation of (I), and acetic anhydride, of the semi-cyclic type (II). The acids of type (I), when heated alone, tend to give hydrocarbons of the semi-cyclic type, migration of the double linking taking place when the carbon dioxide is eliminated.

In some cases the hydroxy-acids themselves cannot always be obtained by the saponification of their esters without undergoing partial hydrolysis to the cyclic ketone and fatty acid:



and in these instances the acids themselves undergo the same change when heated alone, so that the above unsaturated acids cannot be prepared from them by the ordinary methods.

Diazo- and Azo-Compounds.

The controversy, referred to in the last two Annual Reports,³² as to the constitution of diazonium salts, has been continued in the form of a series of polemical papers by Hantzsch³³ and Cain.³⁴ In support of the quinonoid formula proposed by the latter, an analogy is drawn between benzenediazonium chloride (I) and *p*-benzo-

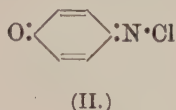
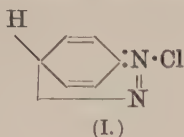
³¹ O. Wallach, *Annalen*, 1909, **365**, 255; *A.*, i, 383.

³² 1907, 120; 1908, 136.

³³ *Ber.*, 1909, **42**, 394, 2137; *A.*, i, 193, 535.

³⁴ *Ibid.*, 1208; *A.*, i, 445.

quinonechloroimide (II), both of which are decomposed by boiling with water, the rupture taking place at the junction of the



nitrogen with the ring. Both compounds are explosive, and react similarly with concentrated hydrochloric acid, yielding chlorobenzene and chlorophenol respectively. The parallel must not be pressed too closely, as it is impossible to regard the formula (I) as that of a typical quinone, but it is suggestive. One objection brought against the new formula, that whilst originally introduced to account for the non-existence of aliphatic diazonium salts it failed to explain the non-existence of simple aliphatic azo-compounds, has since ceased to be valid, owing to the isolation of azomethane, the simplest representative of its class. Hydrazomethane, $\text{CH}_3 \cdot \text{NH} \cdot \text{NH} \cdot \text{CH}_3$, prepared by the hydrolysis of its diformyl derivative, is readily oxidised, and azomethane is obtained as a colourless gas, condensing to a liquid which is pale yellow at 0° , but becomes colourless before solidification, near -78° .³⁵ The compound has considerable stability, which is actually reduced by the introduction of aryl groups, for azotriphenylmethane, $\text{CPh}_3 \cdot \text{N} \cdot \text{N} \cdot \text{CPh}_3$, is found to be incapable of more than momentary existence, decomposing spontaneously into nitrogen and triphenylmethyl.³⁶ Unlike the corresponding derivatives of benzene, the azo-compounds are less stable than the hydrazo-derivatives. Taking into account the character of the known azo-derivatives of substituted fatty acids, it is evident that the presence of aromatic nuclei is unnecessary for the formation of azo-compounds, and the fact that all attempts to prepare diazonium salts in the fatty series have failed, gains considerably in importance.

The great increase in stability conferred on diazonium salts by the introduction of heavy substituting groups³⁷ has been further studied, and it is found that the compounds obtained by diazotising *as*-benzoylmethyl-*p*-phenylenediamine, $\text{NBzMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, are exceedingly stable, even the perchlorate being non-explosive.³⁸ These salts are colourless, but they do not differ in any other respect from the stable coloured salts previously prepared, so that there is no reason to assume any difference of constitution.

³⁵ J. Thiele, *Ber.*, 1909, **42**, 2575; *A.*, i, 560.

³⁶ H. Wieland, *ibid.*, 3020; *A.*, i, 836.

³⁷ *Ann. Report*, 1907, 121.

³⁸ G. T. Morgan and Miss M. Alcock, *Trans.*, 1909, **95**, 1319.

The diazotisation of amines containing strongly acid groups, such as dinitroanilines, is difficult or impossible under ordinary conditions, and a remarkable method of overcoming the difficulty has been discovered, consisting in the use of concentrated nitric acid as the solvent. Nitrous acid being introduced by the addition of a nitrite or of the required quantity of a sulphite, diazotisation proceeds quietly and without secondary reactions, even at so high a temperature as 70°. ³⁹ This fact depends on the great stability of the diazonium nitrates towards nitric acid, a property also observed in the diazotisation of polyhalogen derivatives of *p*-aminodiphenylamine in sulphuric acid, diazonium nitrates being obtained in place of the expected sulphates. ⁴⁰ It is possible to recrystallise these nitrates from hot concentrated nitric acid without decomposition, whilst alcohol immediately eliminates the diazonium group.

It has long been known that amino-derivatives of certain non-benzenoid cyclic systems, namely, antipyrine, triazole, and tetrone acid, are capable of forming diazonium salts. In each of these cases the carbon atom to which the amino-group is attached is doubly linked to a neighbouring atom in the ring (nitrogen in triazole, carbon in antipyrine and tetrone acid). The formulation of the diazonium salt in accordance with Morgan's modification of the quinonoid formula is possible in each instance, the chlorides being:



respectively. ⁴¹

It will be noticed that in all these cases, as in the derivatives of benzene, the carbon atom to which the amino-group is attached is doubly linked to another atom of carbon or of nitrogen. The necessity of such a distribution of residual affinity in the diazotisable molecule may be held to afford a sufficient explanation of the existence of diazonium compounds in certain cases, and their non-existence in others.

No further progress has been made in elucidating the structure of the diazotates, but, on the other hand, the mechanism of coupling in the formation of azo-dyes has been the object of further experiment, with the result of confirming the view ⁴² that the reaction takes place through the intermediate formation of an *O*-azo-derivative. Thus, diazotised *p*-nitroaniline reacts with 2-naphthol-1-sulphonic acid in sodium carbonate solution to form a soluble

³⁹ O. N. Witt, *Ber.*, 1909, **42**, 2953; *A.*, i, 855.

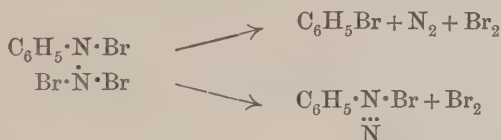
⁴⁰ P. Jacobson, *Annalen*, 1909, **367**, 332; *A.*, i, 683.

⁴¹ M. O. Forster and R. Müller, *Trans.*, 1909, **95**, 2072.

⁴² *Ann. Report*, 1908, 142.

compound, $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, having the same colour as the stable, insoluble azo-compound into which it readily passes by rearrangement.⁴³ A more complex compound, which may also be regarded as an *O*-azo-derivative, is suggested as the cause of the orange colour observed in the formation of "para-nitraniline red" from β -naphthol under certain conditions of alkalinity.⁴⁴ In the coupling of diazotised *p*-phenylenediamine with the amine to form Bismarck brown, $\text{C}_6\text{H}_4[\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2]_2\cdot 4\text{HCl}$, the factor determining the velocity is found by a colorimetric method to be the hydrolysis of the hydrochloride, indicating that the coupling of the diazonium salt takes place with the free amine liberated by hydrolysis. Both amino-groups are diazotised simultaneously.⁴⁵ Reactions of this type evidently lend themselves well to quantitative study.

Further evidence has been obtained in favour of the view, originally suggested and rejected by Kekulé, that the "diazonium perbromides" are really halogen-substituted arylhydrazines. The principal facts in favour of this constitution are (1) the facility with which the perbromides react with ammonia to form diazoimides, (2) their formation from bromine and aromatic hydrazines in acetic acid solution, (3) the formation of unstable additive compounds on the further addition of bromine. The principal evidence for the more generally accepted perbromide formula is the ready decomposition of these compounds into diazonium salts and bromine. In the action of alcohol on these compounds, decomposition takes place in two ways, as indicated by the scheme:



using Blomstrand's formula for the diazonium bromide, the latter compound then decomposing, with the formation of benzene, phenol, and brominated derivatives.⁴⁶

The complete replacement of the hydrazine hydrogen by bromine only takes place in acid solution. In presence of alkalis, a number of different products may be obtained by varying the conditions, but all depend on the progressive substitution of bromine for hydrogen in the hydrazine group, followed by a secondary reaction

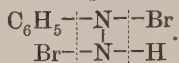
⁴³ H. T. Bucherer, *Ber.*, 1909, **42**, 47; *A.*, i, 193.

⁴⁴ M. Prad'homme and A. Colin, *Bull. Soc. chim.*, 1909, [iv], **5**, 779; *A.*, i, 684.

⁴⁵ V. H. Veley, *Trans.*, 1909, **95**, 1186.

⁴⁶ F. D. Chattaway, *ibid.*, 862.

of the *N*-substituted hydrazine. Thus, the dibromo-derivative undergoes the typical diazo-decomposition, forming bromobenzene:



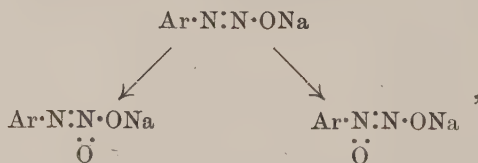
Hydrazobenzene is also formed by the union of two mono-substituted molecules:



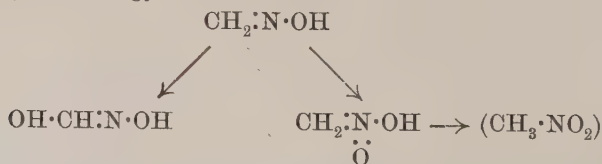
being subsequently converted into azobenzene and diphenyl by the action of the halogen.

In the presence of a large excess of a strong acid, the basic $\cdot\text{NH}_2$ group is saturated, and so protected against substitution, and the $\cdot\text{NH}$ group is then the first to be attacked. The *N*-halogen compound thus produced is of the same type as the acyl halogen amino-compounds, and undergoes rearrangement, under the influence of the acid, to an ortho- or para-halogen derivative, the substituent entering the nucleus in one or other of these positions.⁴⁷

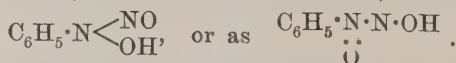
When an alkaline solution of a normal diazohydroxide is oxidised with hydrogen peroxide, the product is a mixture of the salts of a benzenediazoic acid and of a nitrosophenylhydroxylamine:



presenting an analogy to the oxidation of an oxime:



Benzenediazoic acid is to be regarded as phenylnitroamine, $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{NO}_2$, capable also of reacting in the tautomeric form. Nitrosophenylhydroxylamine is also tautomeric, reacting as



The nitrobenzene obtained by the oxidation of a diazotate is entirely a secondary product, formed by the decomposition of nitrosohydroxylamine.⁴⁸

⁴⁷ F. D. Chattaway, *Trans.*, 1909, **95**, 1065.

⁴⁸ E. Bamberger and O. Baudisch, *Ber.*, 1909, **42**, 3568; *A.*, i, 977.

Aniline-black.

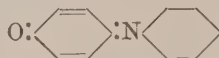
The oxidation of aniline to *p*-benzoquinone by the action of chromic acid, simple as it appears, is a reaction of which the mechanism has been little understood. The explanation usually given, that β -phenylhydroxylamine is first formed, isomeric change to *p*-aminophenol then taking place, followed by oxidation to quinone, is certainly untenable, as phenylhydroxylamine does not pass into aminophenol under the conditions of the experiment. Neither is it possible to consider that the intermediate product is *p*-aminodiphenylamine, as has been suggested by Nover, as the latter compound is not completely convertible into quinone in the cold. The fact, long ago observed, that aniline-black is first formed, has now been utilised as the basis of a complete explanation of the reaction.⁴⁹ Pure aniline-black, prepared by oxidising aniline with only one-quarter of the theoretical quantity of chromic acid, and submitting the product to careful purification, is proved to have the composition $C_{48}H_{36}N_8$. It is quantitatively convertible into *p*-benzoquinone by oxidation with lead peroxide, a reaction indicating that all the aniline residues are united in the para-position. The estimation of the oxygen consumed in its formation shows that the molecule, of eight aniline residues, is three times quinonoid, that is, its formula is:

$NPh \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot NH$,
the position of the two inner quinonoid residues being arbitrarily assumed.

The constitution is confirmed by oxidation with hydrogen peroxide, whereby two atoms of hydrogen are removed, and a fourth nucleus becomes quinonoid. The resulting compound is darker in colour than the less fully oxidised aniline-black, but resembles it in its general properties, and is quantitatively convertible into *p*-benzoquinone. It may be obtained directly from aniline by the use of an excess of a slowly acting oxidising agent. Hydrolysis of either compound removes one-eighth of the nitrogen as ammonia, thus fixing the number of nuclei united in a chain as eight, and compounds containing :O in place of the terminal :NH are obtained, the remainder of the molecule being unchanged. The oxygen derivative of the compound containing four quinonoid groups is the most complete representative of the aniline-black series, as both the base and its salts are dead black, and the change to green on treatment with sulphur dioxide, observed in the lower members of the series, is entirely absent.

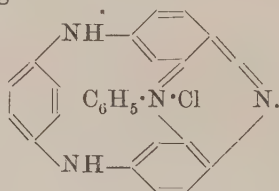
⁴⁹ R. Willstätter and S. Dorogi, *Ber.*, 1909, **42**, 2147, 4118; *A.*, i, 535, 975.

The fact that the yield of *p*-benzoquinone obtained when aniline-black is oxidised with chromic acid does not exceed 85 per cent. is explained by the above formula, the terminal, unsubstituted benzene nucleus being destroyed. The same behaviour is observed in the oxidation of simpler partial quinonoids. Thus, only one-half of the molecule of quinoneanil:



is oxidised by this process, whilst lead peroxide and sulphuric acid convert both rings into *p*-benzoquinone. This difference in the action of the two oxidising agents has proved of value in fixing the constitution of emeraldine and the termolecular imines formed by the polymerisation of quinonedi-imines.⁵⁰ Emeraldine contains none but para-junctions, whilst the termolecular imines contain a single ortho-junction.

H. T. Bucherer⁵¹ has argued that the ready decomposition of indamines by acids, taken together with the stability of aniline-black and emeraldine, excludes the possibility of the formulæ proposed by Willstätter, and an azine formula is preferred. There is, however, no direct evidence for the azine constitution, which is not readily reconcilable with the ultimate complete conversion into *p*-benzoquinone by oxidation. The same objection applies to the closed ring formula proposed by A. G. Green,⁵² which contains both ortho- and para-linkings:



Compounds Exhibiting Ketimino-ename Isomerism or Tautomerism.

A very large class of nitrogenous compounds of both open-chain and cyclic structure owe many of their peculiarities to the circumstance that they contain nitrogen either doubly bound to another atom or attached to one of a doubly bound pair, thus:



This class includes amides, imino-derivatives of ketones and acids, and the more complex series of ureides, cyanic and cyanuric acid, and allied substances, and these show so many characters

⁵⁰ R. Willstätter and H. Kubli, *Ber.*, 1909, **42**, 4135; *A.*, i, 976.

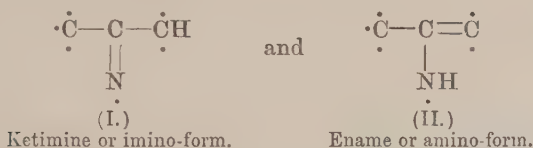
⁵¹ *Ber.*, 1909, **42**, 2931; *A.*, i, 820.

⁵² *J. Soc. Dyers*, 1909, **25**, 188; *A.*, i, 612.

in common that much is to be gained by adopting a suggestion from J. F. Thorpe⁵³ to treat them as closely allied substances. They become "tautomeric" in certain circumstances, if, for example, a hydrogen atom is affixed to the outer doubly bound atom, or this may even occasionally result in a definite dynamic isomerism:



The case where both X and Y are carbon atoms may be discussed first. Thorpe and Best have made a systematic study of these cases, and during the past few years have studied very thoroughly the way in which such substances may be formed and their general properties. They generalise as follows, referring to those which can exist in the two forms:



and to the number of "negative" groups (that is, unsaturated groups of the type $\cdot\text{CN}$, $\cdot\text{CO}_2\text{Et}$, etc.) attached to the carbon atoms to which dots are affixed.

(a) With three or more such groups, the amino-configuration (II) is adopted, and the hydrochlorides at once dissociate with water, regenerating the free amino-compound. (b) With one such group, the compounds assume the structure (I), being true imino-compounds, and the hydrochlorides with water yield ammonium chloride and the corresponding *keto*-compound proper, $\cdot\dot{\text{C}}:\text{C}:\dot{\text{C}}\text{H}$,
 O

(c) With two negative groups, tautomeric or merotropic phenomena occur, and the hydrochlorides are mixed salts of the amino- and imino-types. The conclusions are supported by a mass of convincing experimental evidence.⁵⁴

Compounds closely related to carbamide are receiving much attention, especially as the commercial article, "calcium cyanamide," is a convenient source of some which have hitherto been difficult to prepare in quantity. Dicyanodiamide and guanidine,⁵⁵ for example, are now easily prepared in large quantities. Recent investigations seem to prove that the former is not acidic, and does not form salts, as has been supposed, those previously described being derived

⁵³ *Proc.*, 1909, **25**, 309.

⁵⁴ S. R. Best and J. F. Thorpe, *Trans.*, 1909, **95**, 1506.

⁵⁵ C. Ulpiani, D.R.-P. 209481; *A.*, i, 701.

The Committee on the Medical Education of Women, created by the American Medical Association in 1915, has been working for the purpose of securing the admission of women to the medical profession. The committee has been successful in securing the admission of women to the medical profession in many countries, and it is now working for the admission of women to the medical profession in this country.

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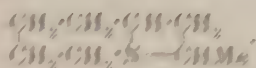
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found definitely in the tissues of the exposed specimens. The exposed and unexposed groups as to occurrence of breast cancer were more or less equal. The only difference between the two groups was the duration. If the exposure is a more typical of occupation, and the length of time between the beginning and the end of study is a series of two years separated by a continuation of time a few weeks. In some cases the structure of the breast is having the structure⁽⁴⁾:



There have been numerous occasions during the past few years when the activities of the press complex have been the subject of public discussion. In the popular press, which is the important mass communication agency, and the press often reported in fact rather than the opinion of fact a serious problem and at various intervals in the past few years the national press is necessary for the execution of public law have been the subject of discussion. The new press complex and program are generally considered completely new and have been the subject of discussion and the official records of the public interest have been regarded by a substantial number of

[illegible]

In order to test the activity of the grouping $\text{MgO} \cdot \text{CaO} \cdot \text{OH}$ anhydrous $\text{Zn}(\text{NH}_4)_2\text{CO}_3$ hydrates, separately a primary sample was examined, but was not found to undergo any decomposition, its activity being much greater than that of the $\text{Zn}(\text{NH}_4)_2\text{CO}_3$.

181, 224, 225, 227.

H. A. D. Jones

* M. Parrywell and P. Tschu, *ibid.*, 1988.

8. H. Vandy, *ibid.*, 1.

1874

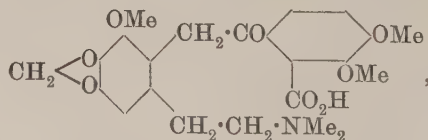
⁶⁶ Ind. 285, 353, 368; A. i. 451, 452.

19. *Chrysomelidae* (continued)

The complete synthesis of papaverine and laudanosine (*N*-methyl-tetrahydropapaverine) has been effected, the former compound being prepared from aminoacetoveratrone and homoveratroyl chloride, followed by reduction and elimination of water.⁶⁷ Papaverine yields tetrahydropapaverine on reduction, and methylation of this converts it into laudanosine.⁶⁸ The latter alkaloid has been directly synthesised by combining homoveratroyl chloride with homoveratrylamine, converting into dihydropapaverine by elimination of water, reducing the methochloride of the latter, and resolving the racemic alkaloid obtained. This is the first complete synthesis of an opium alkaloid.⁶⁹

Narcotine and hydrastine are known to yield cotarnine and hydrastinine respectively when oxidised with manganese dioxide, together with opianic acid. As laudanose behaves in a similar manner, yielding veratraldehyde and a basic degradation product,⁷⁰ other related compounds have been examined, and the reaction is found to be perfectly general for substituted 1-benzyltetrahydro-*isoquinolines*,⁷¹ the aldehyde obtained being that corresponding with the substituted benzyl group. Compounds containing alkyl instead of benzyl do not undergo the change. The reaction is likely to prove valuable in the study of the rarer alkaloids, especially those of the opium group, in which such a structure is probably of frequent occurrence.

The formula for narceine, proposed by Freund and Frankforter, contains the group $\cdot\text{CH}_2\cdot\text{CO}\cdot$, uniting two benzenoid rings. The presence of this group has been confirmed by a comparison of narcindonine with diketo- α -phenylhydrindene.⁷² Narceine, according to the annexed formula, is a derivative of deoxybenzoincarboxylic acid:



and it yields narcindonine by a similar reaction to that by which the parent substance is converted into diketo- α -phenylhydrindene. Narcindonine forms red enolic salts with alkalis, and colourless

⁶⁷ A. Pictet and A. Gams, *Compt. rend.*, 1909, **149**, 210; *A.*, i, 671.

⁶⁸ F. L. Pyman, *Trans.*, 1909, **95**, 1610.

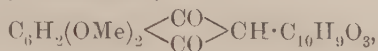
⁶⁹ A. Pictet and Mlle. M. Finkelstein, *Compt. rend.*, 1909, **148**, 925 ; *A.*, i, 323.

⁷⁰ F. L. Pyman, *Trans.*, 1909, **95**, 1266.

⁷¹ F. L. Pyman, *ibid.*, 1738.

⁷² M. Freund and P. Oppenheim, *Ber.*, 1909, **42**, 1084; *A.*, i, 410.

ketonic salts with acids. When its methiodide is heated with sodium hydroxide, narcindone,



is formed.

Constitution of Naturally Occurring Substances.

An inquiry into the nature of the dye employed by the Romans, and generally known as "antique purple," has led to very interesting results. The adrectal glands of species of *Murex* and *Purpura* contain a colourless fluid, which becomes purple or violet on exposure to light. Archæological evidence indicates *Murex brandaris* as the principal source of the dye, and 12,000 individuals of this species were used in the investigation,⁷³ this large quantity yielding 1·4 grams of the crystalline dye. The colouring matter was readily found to be a member of the indigo group, and analysis showed the molecule to contain, most unexpectedly, two atoms of bromine. The properties of the colourless parent substance suggesting that the molecule was doubled in the development of the colour, a symmetrical dibromindigotin was suspected, and a comparison with the four possible isomerides, prepared synthetically, proved the dye to be identical in spectroscopic behaviour, solubility relations, etc., with 6: 6'-dibromindigotin. It dyes wool a reddish shade of violet, which accords with the frequent comparison of the antique purple by classical writers with amethyst, violets, and even with indigo vapour (Pliny). The nature of the colourless parent substance remains undetermined.

Having regard to the occurrence of derivatives of indole in animal excretory products, the presence of an indigo compound, although novel, is comprehensible, but the occurrence of a brominated derivative under such conditions is probably unprecedented.

Substitution of indigotin in the 6: 6'-position favours a red shade, the 6: 6'-dichloro-derivative being also reddish-violet, whilst 6: 6'-dimethoxythiindigotin is even orange-red, the 5: 5'-derivative being violet.

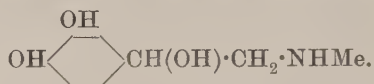
An important investigation of the process of fermentation of indican by its specific ferment, indimulsin,⁷⁴ has thrown much light on the reactions involved, and has accounted for the principal losses in the technical process of extraction, but does not lend itself to summarisation. The "decay" of indoxyl is considerably checked

⁷³ P. Friedländer, *Ber.*, 1909, **42**, 765; *A.*, i, 262,

⁷⁴ A. G. Perkin and F. Thomas, *Trans.*, 1909, **95**, 793; F. Thomas, W. P. Bloxam, and A. G. Perkin, *ibid.*, 824.

by the presence of sulphuric acid during the fermentation. "Indigo-brown" is shown⁷⁵ to be formed by the oxidation of indoxyllic acid, which is very likely to be formed during the fermentation by the action of carbon dioxide on indoxyl.

Important results have been obtained in the group of compounds characterised by their effect in increasing the blood-pressure, the best-known member of the group being adrenaline. This substance is a derivative of catechol, and has the constitution:



The corresponding ketone is also active, and the presence of the methyl group is unessential. It has now been found that the corresponding compounds containing only a single hydroxyl in the para-position are also active. The ketone closely resembles that derived from adrenaline, but the increase in physiological activity brought about by the reduction of CO to $\text{CH} \cdot \text{OH}$ is much less marked when only one hydroxyl is present.⁷⁶ The activity is inhibited by the introduction of methyl into the α - or β -position.⁷⁷

There is a close resemblance between adrenaline and ergot, and an active principle has been isolated from aqueous extracts of the latter substance which exhibits a close chemical, as well as physiological, relationship, namely, *p*-hydroxyphenylethylamine:



The synthetic product, obtained by the reduction of *p*-hydroxyphenylacetonitrile, is proved to be identical with that present in ergot.⁷⁸ The same compound is obtained, in better yield, by acting on anisaldehyde with nitromethane:



reducing the product, and removing the methyl group by means of hydrogen iodide.⁷⁹ The properties of ergot are now fully accounted for by the presence of this base and of ergotoxin.

The β -position of the hydroxyphenyl group in the chain is not essential to the activity of the molecule, for α -*p*-hydroxyphenylethylamine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{NH}_2$, is found⁸⁰ to resemble the β -isomeride in this respect.

⁷⁵ A. G. Perkin, *Trans.*, 1909, **95**, 847.

⁷⁶ F. Tutin, F. W. Caton, and A. C. O. Hann, *ibid.*, 2113.

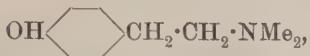
⁷⁷ K. Böttcher, *Ber.*, 1909, **42**, 853; *A.*, i, 152.

⁷⁸ G. Barger, *Trans.*, 1909, **95**, 1123; G. Barger and G. S. Walpole, *ibid.*, 1720.

⁷⁹ K. W. Rosenmund, *Ber.*, 1909, **42**, 4778.

⁸⁰ Tutin, Caton, and Hann, *loc. cit.*

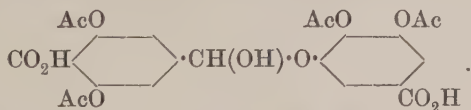
The alkaloid hordenine, obtained from barley, has the constitution:



and is therefore the dimethyl derivative of the ergot base. Methylation of the latter compound leads under all conditions to the formation of hordenine methiodide, and it is not possible to stop the reaction at an intermediate point. The synthesis of hordenine has, however, been effected from phenylethyl alcohol, the chloride from which, treated with dimethylaniline, yields the base, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$, from which the para-hydroxy-derivative required is readily obtained by nitrating, reducing, and boiling the diazo-compound with acid.⁸¹ The physiological action of hordenine was studied by Camus in 1906, and was found to consist in an increase of the blood-pressure, as in the other instances taken from this group.

The fact that phenylethylamine and its substituted derivatives have been recognised amongst the products of digestion, and also amongst the substances formed by the putrefaction of proteins, taken in conjunction with the observations mentioned above, points to the high physiological importance of the group.

The composition of naturally occurring tannin approaches that of a digallic acid, and that constitution is most generally assigned to it, in spite of its optical activity. The natural product is considered by M. Nierenstein⁸² to be a mixture of digallic acid with leucotannin, in which the two rings are united by the group $\cdot\text{CH}(\text{OH}) \cdot \text{O} \cdot$. The penta-acetyl derivative of tannin yields penta-acetyl-leucotannin on reduction, and an additional acetyl group may then be introduced, in accordance with the formula:



The behaviour of the original compound on oxidation is in accordance with the formula proposed. The separation of the constituents of the natural mixture is difficult.⁸³ Methyltannin contains five methoxyl groups, and appears to be a mixture of the pentamethoxy-derivatives of digallic acid and of leucotannin.⁸⁴

⁸¹ G. Barger, *Trans.*, 1909, **95**, 2193.

⁸² *Ber.*, 1909, **42**, 1122, 3552; *A.*, i, 402, 948.

⁸³ L. F. Iljin, *ibid.*, 1731; *A.*, i, 503.

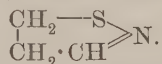
⁸⁴ J. Herzig and V. Renner, *Monatsh.*, 1909, **30**, 543; *A.*, i, 713.

Organic Compounds of Sulphur and Selenium.

A very large amount of important work has been done in this field during the period covered by this report, but for the most part it is of the specialised character, which cannot be dealt with usefully in such a summary, therefore only those points which appear to have a somewhat general interest or applicability have been included.

Hydrogen sulphide acts on dry imino-esters, $R \cdot C \begin{smallmatrix} \searrow OEt \\ \swarrow NH \end{smallmatrix}$, in much the same manner as water does on their hydrochlorides; in ethereal solution the dry gas converts them into ammonia and " β -thion-esters," $R \cdot C \begin{smallmatrix} \searrow OEt \\ \swarrow S \end{smallmatrix}$, which are compounds with rather remarkable properties. They do not yield the thio-acids on hydrolysis, but usually react with ammonia, yielding the corresponding amides, $R \cdot C \begin{smallmatrix} \searrow NH_2 \\ \swarrow S \end{smallmatrix}$, which may therefore occur as secondary products in the preparation of the β -thion-ester.⁸⁵

Thioformamide, $HS \cdot CH : NH \rightleftharpoons S : CH \cdot NH_2$, may be prepared directly from formamide by the action of phosphorus pentasulphide, and appears to be tautomeric in the sense here indicated, and its aqueous solutions are sufficiently acidic to redden litmus. When heated, it yields iminoformyl cyanide, $NH : CH \cdot CN$, and may be converted into thiazole with chloroacetaldehyde, and into a new ring compound, thiazoline (I), with bromoethylamine salts⁸⁶:



The investigation of thio-oxalic acid and its esters has furnished results of very general interest. The esters are obtained by the action of oxalyl chloride on mercaptans, and are usually yellow, crystalline compounds, which react with alcoholic solutions of alkali hydrosulphide, yielding the mercaptan and a salt of thio-oxalic acid, $(COSH)_2$, which, when liberated from its salts, at once decomposes. The salts give characteristic precipitates or colorations with solutions of the salts of heavy metals, particularly of nickel and cobalt.

A remarkable reaction is described by Heiduschka, who has found that ammonia attacks *p*-toluenesulphinic acid in benzene solution in such a manner as to form tolyl disulphoxide and toluenesulphonic acid:



⁸⁵ M. Matsui, *Mem. Coll. Sci. Eng. Kyōto*, 1908, **1**, 285; *A.*, **i**, 463.

⁸⁶ R. Willstätter and T. Wirth, *Ber.*, 1909, **42**, 1908; *A.*, **i**, 459

The acid decomposes in the same manner when melted or boiled with water.⁸⁷

Toluenesulphinic acid is formed when the corresponding sulphonyl chloride is acted on by a solution of sodium arsenite or sulphite, arsenate or sulphate being produced; in order to account for this, the formula $R \cdot SO \cdot OCl$ is proposed for sulphonyl chlorides, and it is surmised that sodium hydroperoxide is formed at an intermediate stage, but as the results seem capable of other and more simple explanations, this suggestion seems unlikely to command confidence unless supported by more direct experimental evidence.⁸⁸

Aromatic sulphinic acids yield ferric salts, which are precipitated even in strongly acid solutions, and are easily filtered and washed, being, moreover, stable in dry air. As they yield ferric hydroxide and sodium sulphinate with sodium hydroxide, the isolation of the sulphinic acids when prepared from the amines by Gattermann's method is most conveniently affected by taking advantage of this property.⁸⁹

The relative instability of the oxidised selenium compounds, as compared with the corresponding sulphur derivatives, is well illustrated in the properties of the analogue of benzenesulphonic acid, namely, benzeneselenonic acid, $C_6H_5 \cdot SeO_3H$, which is easily obtained by heating benzene with selenic acid at 110° . It is so readily reduced that aqueous sulphurous acid converts it into phenyl selenomercaptan if a silver salt is present to fix the latter as it is formed. Even hydrochloric acid is oxidised by it, the product in this instance being benzeneseleninic acid, $C_6H_5 \cdot SeO_2H$.⁹⁰

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⁸⁷ A. Heiduschka, *Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 170; *A.*, i, 144.

⁸⁸ A. Gutmann, *Ber.*, 1909, 42, 480; *A.*, i, 144.

⁸⁹ J. Thomas, *Trans.*, 1909, 95, 342.

⁹⁰ H. W. Doughty, *Amer. Chem. J.*, 1909, 41, 326; *A.*, i, 296.

STEREOCHEMISTRY.

THE present report deals with the progress of stereochemistry during the two years which have elapsed since the last report on this branch of chemistry appeared. Some of the more striking developments which have taken place during this period have been mentioned in the report on Organic Chemistry for 1908, but, in order to secure continuity, it will in some cases be necessary to refer to these again.

The past two years have been marked by great activity on the part of the numerous workers in this most interesting and productive field, and the output of important work has been so great that it is difficult, within the narrow limits of this report, to do justice even to all the work which has an obvious bearing on general progress; consequently a number of researches which have added to the sum of our knowledge must of necessity be left unmentioned.

A good deal of attention has been paid to the problem of effecting a complete asymmetric synthesis, and a number of papers have been published in which an account is given of attempts made to bring this about by the use of circularly polarised light, or of a combination of magnetic and electric fields; hitherto all these attempts have led to negative results, but the use of emulsin for effecting asymmetric synthesis has been made successfully in a number of cases.

The allied problem of separating the synthetic mixture of enantiomorphous isomerides has also attracted attention, and the work of Ostromisslensky has shown it in a new aspect, since it is clear that a separation can be effected without the actual use of one of the enantiomorphs, or even of an optically active substance, but merely by using a substance isomorphous with the active substance.

The attempts to verify experimentally van't Hoff's prediction, that optical activity could be due to enantiomorphism of the molecule without being assignable to a single asymmetric atom, have now been brought to a successful issue. The resolution of two substances of this class has been announced: first, 1-methylcyclohexylidene-4-acetic acid, by Perkin, Pope, and Wallach, and, secondly, 4-oximinocyclohexanecarboxylic acid, by Mills and Miss Bain. In both cases the molecule is devoid of a plane of symmetry, but contains no atom which is asymmetric according

to any of the accepted definitions of an asymmetric atom. The case of 4-oximinocyclohexanecarboxylic acid acquires additional interest on account of its important bearing on the Hantzsch-Werner hypothesis concerning the isomerism of oximes.

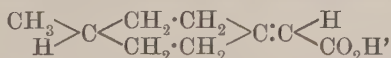
The study of the quantitative relations of optical activity has been the subject of a very large number of communications, the general trend of which has been to demonstrate, first, the importance of the chemical character of the groups in the molecule as distinct from their mass, and, secondly, that the value of the rotatory power is more dependent on the solvent, on temperature, and on the wave-length of the light used than had hitherto been suspected.

The Walden inversion and the closely allied subject of racemisation have received a great deal of attention, and, in regard to the former, the results obtained have complicated matters very considerably by showing that some of the conclusions deduced from Walden's original observations and from Fischer's work in 1907 are not applicable in other cases, but, at the same time, new facts lend support to other conclusions, and these will probably be found universally applicable. Thus it appears that the Walden inversion is dependent on the presence of a carboxyl group attached to the asymmetric carbon atom, and that it is never caused by the action of phosphorus pentachloride.

A very large number of new optically active substances have been prepared, and among them a second compound owing its activity to silicon.

The investigations which have added a new type of molecular structure causing optical activity to those already known may be considered first.

The acid resolved by Marckwald and Meth,¹ melting at 40—41°, and stated by them to be 1-methylcyclohexylidene-4-acetic acid,



has eventually been proved² to be the isomeric 1-methyl-Δ³-cyclohexene-4-acetic acid, whilst the acid prepared by Perkin and Pope and by Wallach, melting at 66°, possesses the structure represented by the above formula.

This acid has been resolved³ by the fractional crystallisation of its brucine salt from dilute alcohol. The complete separation of the two salts was found to be extremely difficult, owing to the formation of mixed crystals of the salts *d*A/B and *l*A/B, but both the active acids have been obtained pure, melting at 52·5—53°, and having $[\alpha]_D \pm 81^\circ$ in 0·7 per cent. solution in absolute alcohol.

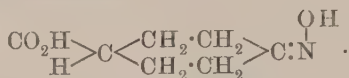
¹ *Ber.*, 1906, **39**, 1171; *A.*, 1906, i, 360.

² See *Trans.*, 1909, **95**, 1791, for references.

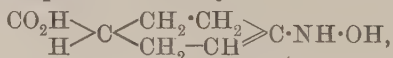
³ Perkin, Pope, and Wallach, *ibid.*, 1789.

The racemic acid melts at 66° , and a mixture of this with one of the active acids can be found melting at as low a temperature as $43-44.5^{\circ}$; hence the melting-point curve for mixtures of the *d*- and *l*-acids must be of the same type as that of the dimethyl tartrates.

Another exceedingly interesting example of a substance owing its activity to enantiomorphism of the molecule has been found in 4-oximinocyclohexanecarboxylic acid,



A preliminary account⁴ only has appeared, in which the resolution of the acid by fractional crystallisation of its quinine salt from ethyl acetate is described. The sodium salt, after removal of the quinine, was found to show a rotation of -4.4° in aqueous solution in a 2-dcm. tube, and this activity was at once destroyed by the addition of acid. Further details of this work will be awaited with interest, since the behaviour of this substance has an important bearing, not only on the demonstration of a new type of molecular structure capable of causing optical activity, but also on the Hantzsch-Werner hypothesis of the stereoisomerism of oximes, which would receive the very strongest confirmation if this acid can be proved to have the structure assigned to it above, and, at the same time, to exhibit optical activity. In this case the molecule can only be devoid of a plane of symmetry if the hydroxyl group attached to the nitrogen atom is deflected to the right or left in the plane of the ring. An alternative formula containing an asymmetric carbon atom seems possible, namely:



but if this were the constitution, it is not easy to understand why acidification should cause the disappearance of activity, whereas this can be explained with the aid of the oximino-formula.

It has long been recognised that molecular asymmetry or enantiomorphism of the molecule is the essential cause of activity, although the asymmetry could usually be referred to a single atom, four valencies of which were occupied in linking four different groups; in the cases mentioned above a somewhat modified definition of an asymmetric atom would include the case of the atom $\begin{array}{c} \text{CH}_3 \\ \text{H} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} \begin{array}{c} \diagdown \\ \diagup \end{array}$

in the first case,^{4a} and $\begin{array}{c} \text{CO}_2\text{H} \\ \text{H} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} \begin{array}{c} \diagdown \\ \diagup \end{array}$ in the second.

The problem of effecting a complete asymmetric synthesis, that is, producing an optically active substance without the aid of another

⁴ W. H. Mills and Miss A. M. Bain, *Proc.*, 1909, 25, 177.

^{4a} See A. E. Everest, *Chem. News*, 1909, 100, 295; *A.*, 1910, ii, 6.

optically active substance, has been attacked vigorously, but hitherto without success.

Several reactions which are influenced by light have been carried out in circularly polarised light; thus, the acids $\text{CN}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ and $\text{CO}_2\text{H}\cdot\text{CClMe}\cdot\text{CClMe}\cdot\text{CO}_2\text{H}$ lose carbon dioxide under the influence of light in presence of uranium salts, yet when the incident light had been passed through a magnetic field the product was inactive.⁵ Similarly, the change of *r*-*o*-nitrobenzaldehydediamyl-acetal in solution in *r*-amyl alcohol into amyl *o*-nitrosobenzoate under the influence of circularly polarised light gave rise to an inactive compound,⁶ and the exposure of copper racemate to circularly polarised light also gave no result.⁷

The experiments first mentioned have been criticised by A. Byk,⁸ who points out, quite correctly, that the combination of ordinary light and a magnetic field would not be expected to give any result, since the light is not circularly polarised.

The union of bromine with methyl fumarate and with methyl cinnamate has also been carried out under the influence of superposed magnetic and electrostatic fields,⁹ but the products were inactive.

A large number of syntheses, which, to distinguish them from the above, may be described as partial asymmetric syntheses, and in which an optically active substance is used, have been carried out. When the union of benzaldehyde and hydrocyanic acid is brought about under the catalytic action of emulsin, *d*-benzaldehyde-cyanohydrin is produced, and from this pure *l*-mandelic acid can be obtained.¹⁰ A number of other aldehydes also give optically active cyanohydrins under the influence of emulsin.¹¹

Emulsin is also found to destroy *d*-benzaldehyde-cyanohydrin more rapidly than its antimeride, so that the latter is in excess when emulsin acts on the synthetic *dl*-mixture.¹²

Syntheses of active substituted glycollic acids have been effected by the action of Grignard's reagent on *d*-amyl pyruvate and on *d*-amyl phenylglyoxylate.¹³ A comparison of the results now obtained with those previously obtained leads to the conclusion that the greater the optical activity of the active group present

⁵ F. Henle and H. Haakh, *Ann. Report*, 1908, 107.

⁶ P. Freundler, *Ber.*, 1909, **42**, 233; *A.*, i, 164.

⁷ A. Cotton, *J. Chim. Phys.*, 1909, **7**, 81; *A.*, ii, 278.

⁸ *Ber.*, 1909, **42**, 141; *A.*, i, 130.

⁹ P. A. Guye and G. Drouguine, *J. Chim. Phys.*, 1909, **7**, 97; *A.*, ii, 278.

¹⁰ L. Rosenthaler, *Biochem. Zeitsch.*, 1909, **14**, 238; *A.*, i, 74; S. J. M. Auld, *Trans.*, 1909, **95**, 927.

¹¹ L. Rosenthaler, *Biochem. Zeitsch.*, 1909, **17**, 257; *A.*, i, 622.

¹² K. Feist, *Arch. Pharm.*, 1909, **247**, 226; *A.*, i, 589.

¹³ A. McKenzie and H. A. Müller, *Trans.*, 1909, **95**, 544.

in a molecule during the asymmetric synthesis the greater is its directive influence on that synthesis. Mandelic acid having $[\alpha]_D -15.6^\circ$ has been obtained by the reduction of *l*-menthyl phenylglyoxylate and subsequent hydrolysis, racemisation during the action of potassium hydroxide having been prevented by acetylation of the hydroxyl group.

Some very interesting observations have been recorded on the separation of *d* + *l*-mixtures of enantiomorphous compounds. Thus, a crystal of *l*-asparagine added to a supersaturated solution of sodium ammonium *dl*-tartrate causes the separation of a quantity of the *d*-tartrate, with which it is isomorphous, and so does a crystal of any alkali salt of *d*-tartaric acid.¹⁴ A crystal of the *l*-tartrate causes the deposit of a crop of levorotatory crystals. Further, it was found that it is not necessary that the nucleating material should itself be active if it be isomorphous with the tartrate, and therefore presumably tetartohedral; thus, a crystal of glycine added to the supersaturated solution of *dl*-asparagine causes a deposit of either the *d*- or *l*-compound, the same crystal always producing a crop of crystals having a rotatory power of the same sign.

These observations afford another method of distinguishing a racemic compound from a *dl*-mixture; from a supersaturated solution of the former the crystals deposited when the solution is nucleated with a suitable material would be inactive, whereas the latter would yield an active deposit under the same conditions.

A large number of experiments on the slow, spontaneous crystallisation of solutions of sodium ammonium *dl*-tartrate were described in 1898, and now further interesting observations on this subject are recorded.¹⁵ When the solutions were allowed to evaporate in the laboratory, the first deposits obtained were usually dextrorotatory; thus, for example, in one series of experiments dealing with nineteen solutions, sixteen gave dextrorotatory deposits; when the solutions were allowed to evaporate in desiccators so as to exclude dust, the proportion of dextrorotatory deposits were smaller, thus in two series of experiments it was 5 to 4 and 11 to 8. It seems therefore probable that the preferential deposition of dextrorotatory material is caused by inoculation by the dust of the laboratory, or by the presence of an extremely minute excess of *d*-tartrate, which is very difficult to remove completely from the racemate. The deposit would naturally be expected to have the same sign of rotation as that of the first crystal actually formed from the solution.

A new aspect of the difficulties attending the resolution of acids and bases by the crystallisation of a salt with an active base or

¹⁴ I. Ostromisslensky, *Ber.*, 1908, **41**, 3035; *A.*, 1908, ii, 913.

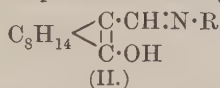
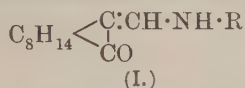
F. S. Kipping and W. J. Pope, *Trans.*, 1909, **95**, 103.

acid has been revealed by experiments that have shown that when a base can be resolved by means of an active acid this active base is not necessarily capable of resolving the *dl*-acid.¹⁶ Thus, *d*-methylhydrindamine was used to resolve *dl*-sulphobenzylethylpropylsiliclyl oxide, but the active acid does not resolve *dl*-methylhydrindamine, and the latter is not resolved by *d*-mandelic acid, whereas either the *d*- or *l*-base is capable of resolving *dl*-mandelic acid.

It is therefore clear that the mixture $dAdB + dAlB$ does not always behave in the same way as $dAdB + lAdB$; one of these pairs may form a partly racemic salt, and therefore the constituents cannot be separated by crystallisation, while the other pair does not, and is therefore separable.

A new method for determining whether a primary or secondary amine is or is not externally compensated has been based on the use of oxymethylenecamphor.¹⁷

The method is identical in principle with that involving the use of an active acid chloride,¹⁸ but is more convenient, since oxymethylenecamphor is readily obtainable. This substance condenses readily with amines to form crystalline compounds of the type (I):



which can be separated into two components if the amine used is externally compensated.

The compounds derived from primary amines usually exhibit marked mutarotation, which, it is suggested, is due to the existence of the dynamic isomerides (I) and (II).

This view is supported by the following facts: first, equilibrium is reached in a few minutes in the presence of a small quantity of sodium ethoxide, and, secondly, the derivative of methylaniline shows no mutarotation.

The compounds derived from *o*- and *p*-nitroanilines do not exhibit mutarotation, whereas that of *m*-nitroaniline does; this, it is suggested, is due to the suppression of one dynamic isomeride by the strongly acidic nitro-group, which is more closely associated with the imino-group in the ortho- and para- than in the meta-derivative.

The case of *ac*-tetrahydronaphthylamine is interesting; the compound from this substance and oxymethylenecamphor appears to be homogeneous, but exhibits mutarotation. These observations can readily be explained on the same assumption as that which was adopted¹⁹ to account for the fact that this substance undergoes

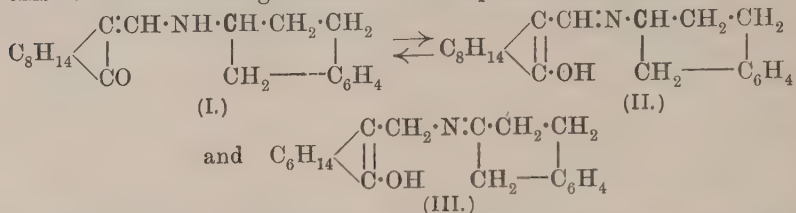
¹⁶ Kipping, *Trans.*, 1909, **95**, 408.

¹⁷ W. J. Pope and J. Read, *ibid.*, 171.

¹⁸ F. S. Kipping and A. H. Salway, *ibid.*, 1904, **85**, 438.

¹⁹ W. J. Pope and A. W. Harvey, *Trans.*, 1901, **79**, 74.

almost complete racemisation when liberated from its salts. In this case the following scheme would represent the changes:



Thus, owing to a tendency for the nitrogen to become doubly linked to the (asymmetric) carbon atom in the ring, the compound (I) is converted into two forms (II and III), of which the latter is no longer asymmetric as regards the tetrahydronaphthylamine part of the molecule, and consequently in solution the *d*-form would be readily converted into the *l*-form and vice versa, and no separation would be effected.

Several amino-acids have been resolved by the action of yeast in the presence of sugar,²⁰ and the optical antimerides of the natural substances have been thus obtained. Thus, *d*-phenylalanine, *d*-serine, *l*-phenylaminoacetic acid (impure), and α -amino- α -methylbutyric acid have been prepared.

Methylisoserine was readily resolved in the form of its benzoyl derivative by means of quinine or brucine,²¹ and the formyl derivative of α -amino-*n*-hexoic acid similarly by the use of brucine.²²

Synthetic α - and β -cincholeuponic acids have been resolved by means of brucine, and *d*- β -cincholeuponic acid, to obtain which the brucine salt of the acetyl derivative was used, is found to be identical with the acid obtained from quinine and cinchonine.²³

In spite of the fact that difficulties have been encountered so frequently in the resolution of sulphonic acids, *dl*-camphorsulphonic acid from synthetic camphor can be resolved readily by means of brucine.²⁴

Our knowledge of racemic, pseudo-racemic, and partly racemic compounds has been extended, for, in addition to the interesting work of Kipping already mentioned, the following observations are recorded.

Tetrahydroquinaldine hydrogen tartrate forms a partly racemic salt above 59°, but below this temperature the two salts are separable by crystallisation.²⁵

The melting-point curve of the *l*-menthyl *d*- and *l*-mandelates

²⁰ F. Ehrlich and A. Wendel, *Zeitsch. Ver. deut. Zuckerind.*, 1908, 198; *A.*, 1908, i, 268.

²¹ F. W. Kay, *Annalen*, 1908, 362, 325; *A.*, 1908, i, 772.

²² D. Marko, *ibid.*, 333; *A.*, 1908, i, 772.

²³ A. Wohl and R. Maag, *Ber.*, 1909, 42, 627; *A.*, i, 254.

²⁴ B. Rewald, *ibid.*, 3136; *A.*, i, 811.

²⁵ A. Ladenburg and W. Herrmann, *Ber.*, 1908, 41, 966; *A.*, 1908, i, 364.

examined in 1907²⁶ showed that a definite partly racemic compound was formed. The solubility in alcohol of *l*-menthyl *dl*-mandelate in presence of each of the *d*- and *l*-mandelates separately has now been examined at different temperatures. The curve is of the ordinary double salt type, and there is no evidence of the existence of a transition point between 35° and -15°.²⁷

Further information concerning the melting-point curves of pseudo-racemic mixtures has been acquired by the study of certain *d*- and *r*-amyl derivatives.²⁸ The melting-point curve of a pseudo-racemic mixture is usually a horizontal straight line, and this is true in the following cases: *d*- and *r*-1-amyl 3-nitrophthalates, the compounds themselves and mixtures of them melting at 116°, *d*- and *r*-2-amyl 3-nitrophthalates melting at 155°, *d*- and *r*-amyl phenylcarbamates melting at 31°, and *d*- and *r*- β -methylvaleramides melting at 126°. The melting-point curve of a pseudo-racemic mixture had been found to show a maximum in the case of the carboximes, and the first instance of a minimum has now been observed in the case of *d*- and *r*-amyl carbamates.

The problem of racemisation, especially when it occurs during chemical transformations, and the allied problem of the Walden inversion continue to attract attention, and many valuable contributions to our knowledge of the mechanism of these processes have to be noted.

It is found²⁹ that if *d*-amyl alcohol is converted into *d*-amyl bromide by means of phosphorus tribromide, the bromide obtained has $[\alpha]_D$ 4.25°, but when hydrobromic acid is used the value of $[\alpha]_D$ is only 3.68°. Therefore partial racemisation occurs during the action of hydrobromic acid. If now *d*-amyl bromide is converted into *d*-amyl acetate by the action of silver acetate at 150°, and the latter hydrolysed by means of 22 per cent. sodium hydroxide solution, the amyl alcohol obtained shows a rotation of only -1.08° in a 5 cm. tube instead of -2.29°. The racemisation has not taken place during the hydrolysis of the *d*-amyl acetate, since if this is prepared directly from the alcohol and acid and hydrolysed, the alcohol is recovered with unchanged rotation. Further, if the *d*-amyl bromide is converted into the iodide, and the latter into the acetate by the action of potassium acetate, the amyl alcohol obtained on hydrolysis has a rotatory power of -2.13°, whereas if silver acetate is used instead of potassium acetate, the alcohol obtained finally has a rotatory power of -1.53°. The racemisation therefore takes place during the action of silver acetate on the bromide, and, to a less extent, on

²⁶ *Ann. Report*, 1907, 185.

²⁷ A. Findlay and Miss E. M. Hickmans, *Trans.*, 1909, 95, 1386.

²⁸ W. Marckwald and E. Nolda, *Ber.*, 1909, 42, 1583; *A.*, i, 350.

²⁹ W. Marckwald and E. Nolda, *loc. cit.*

the iodide. This case therefore closely resembles the Walden inversion.

Another case which resembles the Walden inversion was found in the action of nitrous acid or of nitrosyl bromide on active phenyl-aminoacetic acid, when inactive mandelic or phenylbromoacetic acid was produced. It is noteworthy that in this case racemisation was almost complete when the ethyl ester of the active amino-acid was used.³⁰

The study of *l*-benzoin and its derivatives has revealed a number of cases in which racemisation takes place very readily.³¹ *l*-Benzoin itself is stable in the cold, but is rapidly racemised in presence of an alkaline catalyst; its methyl and ethyl ethers show the same behaviour, the former being completely racemised in the cold by a 0.113*N*-solution of alcoholic potash in five minutes. The ethers are also racemised by heat.

The racemisation in these cases is readily explained by keto-enolic change taking place, thus:



This view is supported by independent evidence³² that benzoin can react as the enolic form.

The change of *l*-pinene into dipentene under the influence of aqueous-alcoholic sulphuric acid has been examined, and it has been shown that active terpineol and an ether are first formed; these are then converted into *l*-limonene and then finally into dipentene.³³

A similar case of almost complete racemisation was observed when synthetic active terpineols were dehydrated by the action of magnesium methyl iodide in the cold, or of anhydrous oxalic acid at 100°; the dipentene produced showed a specific rotatory power of only 5°.³⁴

The change of *l*-amygdalin into a mixture of unequal quantities of *d*- and *l*-amygdalin (the prefixes *d*- and *l*- here indicate the character of the mandelic acid obtainable from the amygdalin) has been shown to be brought about by the catalytic action of alkalis, but the change³⁵ is complicated.

A brief summary of our knowledge of the Walden inversion was given in 1907,³⁶ including the work done during that year by

³⁰ E. Fischer and O. Weichhold, *Ber.*, 1908, **41**, 1286; *A.*, 1908, i, 419.

³¹ H. Wren, *Trans.*, 1909, **95**, 1594.

³² W. N. Haworth, *ibid.*, 486.

³³ W. A. Smirnoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 996; *A.*, i, 942.

³⁴ K. Fisher and W. H. Perkin, jun., *Trans.*, 1908, **93**, 1871.

³⁵ J. W. Walker and V. K. Krieble, *Trans.*, 1909, **95**, 1435.

³⁶ *Ann. Report*, 1907, 190. A more detailed historical account was given by A. McKenzie and G. W. Clough, *Trans.*, 1908, **93**, 811.

Fischer. It appeared then that the following statements were justified.

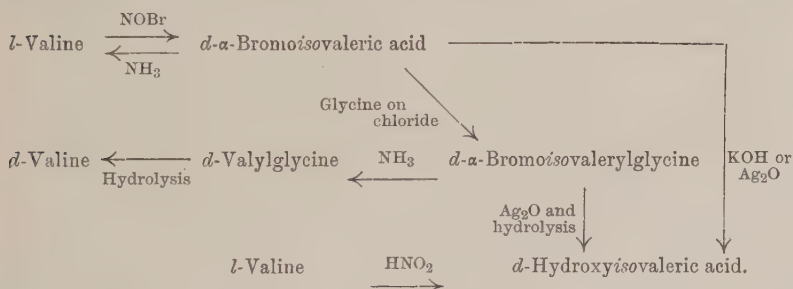
(1) The inversion is dependent on the presence of a carboxyl group attached to the asymmetric carbon atom, and does not take place when the CO_2H group has been converted into CO_2Et or $\text{CO}\cdot\text{NHR}$.

(2) Phosphorus pentachloride, ammonia, nitrous acid, and potassium hydroxide seem to be optically normal in their action, that is, they do not produce inversion, whereas silver oxide and nitrosyl bromide are optically abnormal.

Evidence was also produced showing the probability that the Walden inversion was preceded by the formation of additive compounds, and actually took place during the molecular turmoil attending the breakdown of these complexes.

Subsequent work confirms the first conclusion, but has so altered the second that it is now applicable only to phosphorus pentachloride and nitrosyl bromide.

The first of the observations which introduced disorder into an apparently orderly arrangement was made on *l*-valine,³⁷ with which the following transformations were effected:



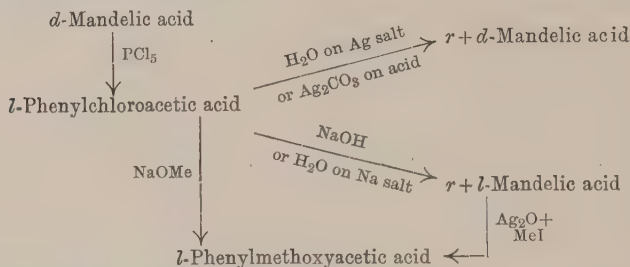
A consideration of the above series of changes shows conclusively that, in this case, ammonia and nitrosyl bromide act in the same way, and so also do potassium hydroxide and silver oxide, whereas in all cases previously examined these reagents acted differently, and, apparently, potassium hydroxide and ammonia were normal in their action while nitrosyl bromide and silver oxide were abnormal.

It seems probable that, in this case, ammonia behaves abnormally, and silver oxide normally, since the behaviour of ammonia is different while that of silver oxide is the same when the carboxyl group is protected by being converted into a $\text{CO}\cdot\text{NHR}$ group.

Nitrous acid also appears to depart from its usual habit, and to behave abnormally. It is suggested that the differences are due to the *isopropyl* group.

³⁷ E. Fischer and H. Scheibler, *Ber.*, 1908, **41**, 889, 2891; *A.*, 1908, i, 324, 857.

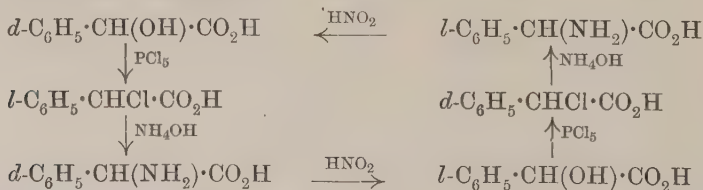
A study of the transformations of active mandelic acid and allied substances³⁸ has shown that the phenyl group also exerts a distinct influence on the course of the Walden inversion, and it certainly favours the occurrence of extensive racemisation during the changes. The following scheme summarises the first series of transformations which were studied:



The action of phosphorus pentachloride on the esters of *d*-mandelic acid yields the esters of *l*-phenylchloroacetic acid, and therefore it is highly probable that this action is optically normal. Consequently the action of silver oxide is also normal, while that of sodium hydroxide is abnormal; thus, the rule which applies in the case of derivatives of malic and propionic acids is reversed here.

It is also concluded that, of the two methylating agents used, sodium methoxide is the one which causes a Walden inversion.

Transformations effected by means of ammonia and of nitrous acid have also been studied by the same workers, and these may be summarised as follows:



As pointed out already, almost complete racemisation takes place during the action of nitrous acid on phenylaminoacetic acid, and this is also true for the action of phosphorus pentachloride and of ammonia, so that the products examined in these cases have only a very feeble rotatory power.

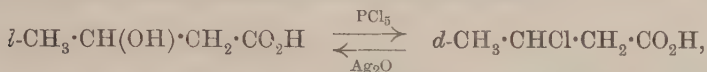
The action of nitrosyl bromide on *l*-phenylaminoacetic acid was also examined, and produced *r* + *d*-phenylbromoacetic acid.

A consideration of the above transformation of *d*- into *l*-mandelic acid shows that a Walden inversion takes place either at one of the three stages or at all three, and that nitrosyl bromide and ammonia behave in the same way. The simplest assumption to make is that

³⁸ A. McKenzie and G. W. Clough, *Trans.*, 1908, **93**, 811; 1909, **95**, 777.

the action of ammonia is abnormal here as it is in the case of α -bromoisovaleric acid.

No Walden inversion takes place when the asymmetric carbon atom is in the β -position with respect to the carboxyl group, since the following transformations have been effected ³⁹:



and the same result is obtained if the methyl ester is used.

The Walden inversion is therefore a complicated process, the course of which is not determined entirely by the mode of action of the reagent used, but is largely influenced by the group attached to the asymmetric carbon atom, since, for instance, the action of ammonia on a halogen acid produces inversion when a phenyl or isopropyl group is attached to the asymmetric carbon atom, and does not when a methyl group or a $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ group is present instead.

The following conclusions, however, have been firmly established by the recent work.

(1) The Walden inversion is dependent on the presence of a carboxyl group attached to the asymmetric carbon atom, and does not take place when the carboxyl group has been converted into $\cdot\text{CO}_2\text{R}$ or $\cdot\text{CO}\cdot\text{NH}\cdot\text{R}$.

(2) The action of phosphorus pentachloride is normal, while that of nitrosyl bromide is abnormal.

A large number of new substances exhibiting optical activity have been prepared in addition to those already mentioned, but many of these must be left unmentioned. Reference has been made to the preparation of optically active terpineols ⁴⁰ and of *l*-benzoin ⁴¹ in the Annual Report for 1908. A number of derivatives of *l*-benzoin have now been prepared, including its methyl and ethyl ethers, carbanilido-*l*-benzoin, and the α -oxime; *d*-benzoin has also been prepared.⁴² The α -oxime of *l*-benzoin exhibits marked mutarotation when dissolved in acetone, acetophenone, or benzaldehyde, but the rotatory power does not change in solution in chloroform, alcohol, or ethyl benzoate. It is suggested that the great increase of rotatory power observed is due to the partial conversion of the α -oxime into the β -oxime, but this could not be isolated.

Two inactive forms of $\alpha\alpha'$ -dihydroxyadipic acid are known; under the action of heat one of these, melting at 146° , gives a dilactone; the other, melting at 174° , gives a lactone-lactide. A study of the configurations of these acids shows that the internally compensated

³⁹ E. Fischer and H. Scheibler, *Ber.*, 1909, **42**, 1219; *A.*, i, 359.

⁴⁰ *Ann. Report*, 1908, 98.

⁴¹ *Ibid.*, 109.

⁴² H. Wren, *Trans.*, 1909, **95**, 1583

(meso) form should give a lactone-lactide, and the externally compensated form should give the dilactone, and this prediction has been verified by the resolution of the isomeride, melting at 146° , into its optically active components by means of cinchonine.⁴³ The isomeride melting at 174° could not be resolved by the same method.

The two optically active forms of thiolactic acid have been isolated by reduction of the corresponding dithiodilactic acids, which were separated by means of *d*- and *l*- α -phenylethylamine.⁴⁴ The thiolactic acids exhibit a very much greater rotatory power, $[\alpha]_D \pm 45.5^\circ$, than the lactic acids.

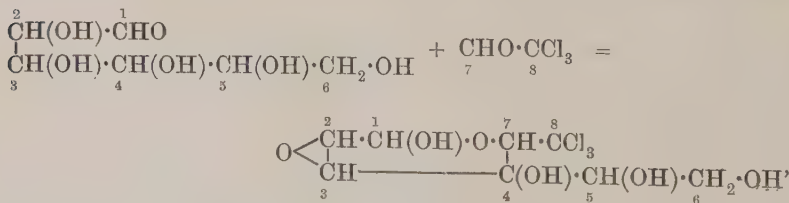
The active prolines have been separated by the crystallisation of the strychnine salts of their *m*-nitrobenzoyl derivatives.⁴⁵

Natural *l*-serine has been converted into the corresponding chloro-acid, and this, when treated with barium hydrosulphide at 100° , and the product oxidised by atmospheric oxygen in presence of ammonia, yields cystine, having $[\alpha]_D -210^\circ$, while natural cystine has $[\alpha]_D -224^\circ$, and the two are therefore the same, allowing for small quantities of impurity in the synthetic product.⁴⁶

It is interesting to note that the two optically active methyl hydrogen mesotartrates have been separated by the crystallisation of their strychnine salts.⁴⁷

The study of optically active reduced naphthoic acids has now been completed by the resolution of Δ^3 -dihydro-2-naphthoic acid by means of menthylamine.⁴⁸ The value of $[M]_D$ for the acid in solution in chloroform is less than that of Δ^2 -dihydro-1-naphthoic acid, but it shows a greater rotatory power than this in solution in benzene. For the purposes of comparison, phenylallylacetic acid, α -phenylvaleric acid, and β -phenyl- α -ethylpropionic acid have also been resolved by means of menthylamine.

Some interesting contributions have been made to our knowledge of the sugar group, including a new method for determining the configuration of three out of the four asymmetric carbon atoms in



⁴³ H. R. Le Sueur, *Trans.*, 1908, **93**, 716.

⁴⁴ J. M. Lovén, *J. pr. Chem.*, 1908, [ii], **78**, 63; *A.*, 1908, i, 714.

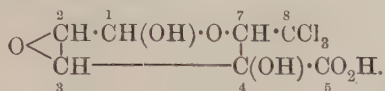
⁴⁵ E. Fischer and G. Zemplén, *Ber.*, 1909, **42**, 2989; *A.*, i, 793.

⁴⁶ E. Fischer and K. Raske, *Ber.*, 1908, **41**, 893; *A.*, 1908, i, 325.

⁴⁷ W. Marckwald and L. Karczag, *Ber.*, 1909, **42**, 1518; *A.*, i, 361.

⁴⁸ R. H. Pickard and J. Yates, *Trans.*, 1909, **95**, 1011.

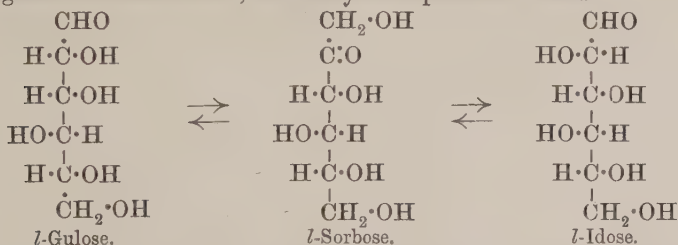
aldohexoses.⁴⁹ Sugars combine with chloral to produce compounds called chloraloses (see equation on p. 122), which on oxidation give chloralic acids of the formula:



The isomerism of the latter depends on the configuration of the three asymmetric atoms numbered 2, 3, and 4 in the original sugar. If, therefore, two sugars give the same chloralic acid, the configuration of these three carbon atoms must be the same.

It is probable, however, that difficulties would arise in the application of this method, owing to the production of two new asymmetric carbon atoms, 1 and 7, during the formation of the chloralose, and it is probable therefore that this would be a mixture in all cases, and, even if one constituent predominated to a large extent, this would not necessarily be the same from two sugars, such as dextrose and *d*-mannose.

An interesting addition has been made to our knowledge of the action of alkalis on sugars. Since dextrose and *d*-mannose are converted by the action of alkalis into lævulose, and a similar change takes place in the case of *d*-galactose, it was to be expected that *l*-gulose and *l*-idose would yield *l*-sorbitose under the same treatment, and it has been shown that this change is effected by baryta.⁵⁰ The change is precisely analogous to the well-known changes mentioned above, and may be represented thus:



The four sugars, *l*-gulose, *l*-idose, *d*-talose, and *l*-ribose, have been purified by conversion into various substituted phenylhydrazones and recovering the sugars by treatment with formaldehyde or benzaldehyde. The last was obtained in a crystalline state when recovered from its *p*-bromophenylhydrazone⁵¹; it has $[\alpha]_D$ 18.8°, and shows no mutarotation.

The polyhydric alcohols, *d*-talitol⁵² and β -glucoheptitol,⁵³ have

⁴⁹ M. Hanriot, *Compt. rend.*, 1909, **148**, 487 and 640; *A.*, i, 206, 287.

⁵⁰ W. Alberda van Ekenstein and J. J. Blanksma, *Rec. trav. chim.*, 1908, **27**, 1; *A.*, 1908, i, 136.

⁵¹ *Idem.*; *Chem. Weekblad*, 1908, **5**, 577; *A.*, 1908, i, 951; *ibid.*, 1909, **6**, 373; *A.*, i, 456.

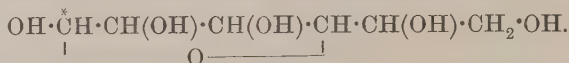
⁵² G. Bertrand and P. Bruneau, *Compt. rend.*, 1908, **146**, 482; *A.*, 1908, i, 249.

⁵³ L. H. Philippe, *ibid.*, 1908, **147**, 1481; *A.*, i, 136.

been prepared in a pure crystalline state by the reduction of *d*-talonic acid and β -glucoheptose respectively.

An interesting relation has been worked out between the rotatory powers of the two dynamic isomerides of aldoses and those of the α - and β -glucosides of the same sugar.⁵⁴

It is assumed that the two forms of a sugar are stereoisomerides on the Tollens' formula, just as the glucosides are:



Then it is found (1) that the difference between the values of $[\text{M}]_D$ of the α - and β -forms of all the aldehydic sugars, and of all their derivatives in which the terminal asymmetric carbon atom (marked *) is not affected, is a nearly constant quantity, and (2) that the sum of the values of $[\text{M}]_D$ for derivatives of the α - and β -forms, in which only the terminal carbon atom is affected, is equal to the sum of the values of $[\text{M}]_D$ for the two forms of the sugar.

If the contribution of the terminal carbon atom to the value of $[\text{M}]_D$ be represented by A, and that of the other asymmetric carbon atoms by B, then the $[\text{M}]_D$ for the α - and β -forms will be represented by (A + B) and (-A + B), and the difference will be 2A, which is approximately the same for all sugars, since the other asymmetric atoms seem to have little influence on the rotatory power of the terminal carbon atom.

For the corresponding glucosides the values of $[\text{M}]_D$ would be +A' + B and -A' + B, since the terminal carbon atom is the only one affected, and the sum (2B) should be the same as that for the α - and β -forms of the sugar.

The following numerical data selected from those given will show the degree of agreement obtained, which is only approximate.

The differences between the values of $[\text{M}]_D$ for α - and β -forms are as follows: Glucose, 160; galactose, 157; arabinose, 162.

The sum of the values of $[\text{M}]_D$ for α - and β -glucoses is 232.

“ “ “ “ α “ β -methylglucosides is 243.
“ “ “ “ α “ β -ethylglucosides is 252.

A very large number of papers dealing with the quantitative study of optical rotatory power have appeared, and the result has been to establish still more clearly the complicated nature of the problem. Many factors must be taken into account besides the masses of the group attached to the asymmetric carbon atom, and in some cases the chemical character of a group entirely outweighs the influence of its mass. This was quite clearly shown by Betti's work in 1907,⁵⁵ and several investigations now supply further instances of a similar kind.

⁵⁴ C. S. Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 66; *A.*, i, 135.

⁵⁵ *Ann. Report*, 1907, 179.

D. A. Chardin and S. Sikorsky⁵⁶ give the details of the examination of derivatives of active amyl and hexyl alcohols undertaken with the view of determining the value of the "atomic product of asymmetry." Fairly consistent values for the atomic product for oxygen can be obtained in this way; thus, the value 129 is obtained from hexyl alcohol, and 132 from amyl alcohol, while theory requires 139. No explanation can be offered of the fact that the sign of the quantity deduced from the two alcohols is different. The values obtained for bromine are, however, much more divergent, and tend to show the limited applicability of the method.

A claim has been made⁵⁷ that the simplified expression $(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)$ gives values for the asymmetry product in better agreement with the actual values of $[M]_D$ found for forty-two derivatives which were examined; but this is controverted very successfully in a later paper,⁵⁸ in which it is shown also that no "rotation equivalents" can be assigned to each group. Assuming the above expression to apply, it is shown mathematically that in a case like that of mandelic and phenylchloropropionic acids the ratio of the values of $[M]_D$ for the methyl and ethyl esters of these two acids should be the same, while the actual ratios found are 0.535 and 1.060 respectively.

Two cases are recorded in which considerable rotatory power is exhibited by compounds in which two of the groups attached to the asymmetric atom have the same weight and differ only in constitution. Thus, cyanopropylisopropylacetic acid was resolved by means of its brucine salt, and found to have $[M]_D$ 182° in toluene solution.⁵⁹ *p*-Tolylbenzylmethylallylammonium hydrogen *d*-tartrate was resolved, and the basic ion was found to exhibit a molecular rotatory power of 246°, which is considerably greater than that of the compounds containing the phenyl and *p*-bromophenyl group in place of the *p*-tolyl group.⁶⁰

A number of papers deal with the influence of unsaturation on rotatory power, but, although it is found that the introduction of an ethylene linking usually increases the value of the rotatory power, this is by no means always the case.

The results obtained with bornyl, menthyl, and amyl esters of phenylpropionic, cinnamic, and phenylpropionic acids are discussed,⁶¹ but no general conclusion can be deduced from them, and it is clear that the influence of unsaturation is in many cases small.

⁵⁶ *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 592; *A.*, 1908, ii, 548; *J. Chim. Phys.*, 1908, **6**, 179 and 584; *A.*, 1908, ii, 470 and 912.

⁵⁷ E. Bose and F. A. Willers, *Zeitsch. physikal. Chem.*, 1909, **65**, 702; *A.*, ii, 361.

⁵⁸ J. W. Walker, *J. Physical Chem.*, 1909, **13**, 574; *A.*, ii, 846.

⁵⁹ E. Fischer and E. Flatau, *Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 876; *A.*, i, 628.

⁶⁰ R. W. Everatt and H. O. Jones, *Trans.*, 1908, **93**, 1789.

⁶¹ T. P. Hilditch, *Trans.*, 1908, **93**, i.

The menthyl esters and brucine salts of a series of nine saturated dibasic acids have also been examined, and here also the influence of constitution is not very marked. In the case of the esters, the rotation of the oxalate is the greatest (-378°), and that of the adipate is next in order of magnitude (-352°), while that of the sebacate is least, 319° . The results with the salts are almost parallel, with the exception of the oxalate, which has the smallest rotatory power.⁶²

The influence of contiguous, unsaturated groups on optical activity is discussed⁶³ and examined in the case of some aromatic esters and salts of camphoric and β -camphorsulphonic acids, and the conclusion is drawn that contiguity of unsaturated groups produces abnormal effects on the optical rotatory power. In both the last-mentioned cases, the original papers should be consulted, since an adequate account of this work cannot be given here.

An account has appeared of an extensive investigation⁶⁴ of the effect of replacing a methyl group or hydrogen atom in an acid by a phenyl group on the rotatory power of the menthyl esters, and the following conclusions are drawn from the results.

(1) The replacement of a methyl group by a phenyl group is usually accompanied by a decrease of rotatory power, as, for example, menthyl crotonate has $[\alpha]_D^{20} -91^\circ$, while menthyl cinnamate has $[\alpha]_D^{20} 77^\circ$

This conclusion does not appear to be justified from the data given, since the values of molecular rotatory power should be compared; these are 204° and 220° respectively. Further, this conclusion is not in agreement with the results obtained with many other compounds, or with those on substituted bornylamines mentioned later, and it is not borne out by the results quoted below.

(2) The assemblage of electronegative (phenyl) groups near the asymmetric system decreases the rotatory power; thus, menthyl β -phenylcinnamate has $[M]_D -137^\circ$, and menthyl α -phenylcinnamate $[M]_D -193^\circ$, compared with 220° for menthyl cinnamate.

(3) The influence of the phenyl group increases as it becomes more distant from the asymmetric system. A comparison of the following three pairs of substances does not, however, appear to bear out this conclusion:

	$[M]_D^{20^\circ}$.	Difference.
Menthyl propionate	-160°	
„ phenylacetate	191	$+31^\circ$
„ butyrate	160	
„ β -phenylpropionate.....	169	$+9$
„ hexoate	165	
„ δ -phenylvalerate	107	-58

A number of acyl-bornylamines have been prepared and their

⁶² T. P. Hilditch, *Trans.*, 1909, **95**, 1578.

⁶³ T. P. Hilditch, *Ibid.*, 331.

⁶⁴ H. Rupe, *Annalen*, 1909, **369**, 311; *A.*, i, 927.

rotatory powers examined⁶⁵ in solution in methyl and ethyl alcohols, in glacial acetic acid, and in pyridine. The compounds now examined, taken in conjunction with the alkylbornylamines examined by Forster,⁶⁶ enable an interesting comparison to be made.

The introduction of an alkyl group into bornylamine increases the dextrorotatory power very considerably, but the difference between the rotatory powers of the various alkyl compounds is not very striking. All the acyl compounds, on the other hand, are levorotatory. The aliphatic acyl derivatives have very different rotatory powers in the different solvents, the order of magnitude being ethyl alcohol, methyl alcohol, acetic acid, pyridine, but the influence of pyridine on the rotatory power of formobornylamide is apparently abnormal. In the aliphatic acyl series, a maximum is found either at the acetyl or the propionyl member in the different solvents.

The members of the aromatic acyl series of compounds are also levorotatory, except in certain cases in pyridine solution, when the compounds become dextrorotatory. The nitrobenzobornylamides are more strongly levorotatory than the toluobornylamides, and the relation between the rotatory powers of the ortho-, meta- and para-compounds is, in some cases, in agreement with theoretical predictions. The original paper should be consulted for the detailed discussion of the results.

The study of certain derivatives of camphorquinone⁶⁷ has led to the production of substances of enormous rotatory power, and to interesting results showing the great influence of unsaturation and of chemical character of the groups present on rotatory power.

Camphorquinone condenses readily with aromatic amines to give compounds of the type $C_8H_{14} \begin{smallmatrix} \diagup C \cdot N \cdot R \\ | \\ CO \end{smallmatrix}$, and with diamines to give compounds containing two camphorquinone residues.

The results obtained by a study of the rotatory powers of the compounds in pyridine or chloroform solutions bring out the following principles illustrated by the compounds the formulæ and molecular rotatory powers of which are given below.

A conjugated double bond (*a*) acting alone produces a small increase in rotatory power; (*b*) while in co-operation with a benzene ring its influence is greatly increased.

(*a*) is illustrated by a comparison of the rotatory powers of 1 and 2, and of 5 and 6, while (*b*) is illustrated in the same way by comparing the difference between 1 and 2 with that between 3 and 4, and the difference between 5 and 6 with that between 7 and 8.

⁶⁵ P. F. Frankland and F. Barrow, *Trans.*, 1909, **95**, 2017 and 2026.

⁶⁶ *Trans.*, 1899, **75**, 934.

⁶⁷ M. O. Forster and T. Thornley, *ibid.*, 1909, **95**, 942.

cases there is a maximum of rotatory power in the green, while there is a minimum in the last case.

The coloured xanthates and xanthogenides of menthol and borneol have also been shown to exhibit anomalous rotatory dispersion in the neighbourhood of their absorption bands.⁷⁰

The investigation of the rotatory power of ethyl tartrate in different solvents has been considerably extended by Patterson and his colleagues.

The rotation in fatty halogen derivatives⁷¹ and in aromatic halogen derivatives⁷² has been examined without any very striking results, but the study of aromatic nitro-derivatives⁷³ has yielded the most remarkable results yet obtained. The specific rotatory power of ethyl tartrate in α -nitronaphthalene at infinite dilution is $+65^\circ$, while in *s*-trinitrobenzene under the same conditions it is -30° , thus surpassing both the upper and the lower limits previously observed, in formamide $+30.4^\circ$, and in ethylene dibromide -19° . The dependence of rotatory power on temperature was also investigated, and it has been found that in one solvent the temperature at which a maximum rotatory power occurs is apparently independent of the concentration. A relationship has been established between the maximum rotatory power and the temperature at which it occurs, which relationship appears to be independent of the nature of the solvent and of the concentration. The lævoro-rotatory power of ethyl tartrate in acetylene tetrabromide decreases very rapidly with increasing temperature, until above 80° the solution becomes dextrorotatory.

Quinoline and benzaldehyde have also been added to the list of solvents examined.⁷⁴ Solutions of ethyl tartrate in the former show a very marked maximum of specific rotatory power of 29° , when the concentration is represented by 44 per cent. of ethyl tartrate, which roughly corresponds with two molecular proportions of quinoline to one of ethyl tartrate. It must, however, be noted that the concentration at which the rotatory power is a maximum is not the same at different temperatures.

The influence of mixed solvents on the rotatory power of ethyl tartrate has also been examined,⁷⁵ the solvents chosen, ethylene dibromide and nitrobenzene, having widely different effects on the rotatory power of the solute, ethyl tartrate, and also very different densities. The influence of each solvent on the rotatory power was

⁷⁰ L. Tschugaeff, *Ber.*, 1909, **42**, 2244; *A.*, ii, 631.

⁷¹ T. S. Patterson and D. Thomson, *Trans.*, 1908, **93**, 355.

⁷² T. S. Patterson and D. P. McDonald, *ibid.*, 936.

⁷³ T. S. Patterson, *ibid.*, 1836.

⁷⁴ T. S. Patterson and D. P. McDonald, *Trans.*, 1909, **95**, 321.

⁷⁵ T. S. Patterson and H. H. Montgomerie, *ibid.*, 1128.

found to be proportional to its volume, and it was possible to calculate the rotatory power of the solutions from their compositions and the known influence of each solvent separately on the rotatory power of the solute.

The method of applying the change in the rotatory power which ethyl tartrate undergoes in different solvents to the investigation of intramolecular change in inactive substances mentioned in 1907⁷⁶ has now been further extended.⁷⁷ The change of piperonal*syn*-oxime, anissynaldoxime, and ω -isonitrotoluene into their dynamic isomerides has been studied, and it has been found that the rate at which these changes proceed is an exceedingly sensitive test for the purity of the ethyl tartrate. The change of ammonium thiocyanate and ammonium cyanate did not seem to proceed so regularly as the others. It is possible that this may be due to interaction of the ethyl tartrate with these substances.

Whether we shall ever be able to unravel the complicated problems of the relation between rotatory power and chemical constitution and of the influence of solvents on rotatory power is doubtful at present; but it is clear from what has been said above that much more experimental work will be required before we can even fix upon the data which are to serve as a basis for theoretical discussion, since, if phenomena like those already mentioned are exhibited, it is useless to attempt to discover general laws or to found a theory on the results obtained with light of one wavelength until it has been proved that anomalous rotatory dispersion is not exhibited by the substances or solutions under examination.

The most important contributions to our knowledge of optical activity of silicon and nitrogen compounds have already been mentioned in 1908,⁷⁸ so that a brief reference must suffice here.

A second asymmetric silicon compound, of the same type as the first resolved in 1907, has now been resolved.⁷⁹ This compound, *dl*-sulphobenzylethylisobutylsilicyl oxide, was again resolved by the use of methylhydrindamine, and the two *d*- and *l*-sodium salts were found to have specific rotatory powers of $\pm 10.5^\circ$, which is nearly twice as great as that shown by the corresponding compound containing the propyl instead of the isobutyl group. The differences between salts of *l*-menthylamine, of bornylamine, or of cinchonine with the two acids are again very slight.

No compound containing a single asymmetric silicon atom has yet been resolved, although in the case of *dl*-benzylethylpropylisobutylsilicanesulphonic acid indications were observed that resolution was

⁷⁶ *Ann. Report*, 1907, 184.

⁷⁷ T. S. Patterson and A. McMillan, *Trans.*, 1908, **93**, 1041.

⁷⁸ *Ann. Report*, 1908, 108, 109, 175.

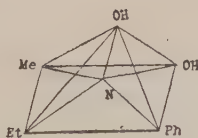
⁷⁹ F. S. Kipping and B. D. W. Luff, *Trans.*, 1908, **93**, 2090.

being effected by crystallisation of the cinchonine hydrogen salt, which gave two fractions of specific rotatory power, $+57.1^\circ$ and $+73.8^\circ$, and this observation is being pursued.⁸⁰

A new type of nitrogen compound exhibiting optical activity has been found in methylethylaniline oxide.⁸¹ The *d*-bromocamphorsulphonate of this base was resolved, and from the solution of the less soluble, *d*A/B, salt the picrate was precipitated and converted into the chloride by treatment with hydrochloric acid. The chloride, $\text{NMeEtPhCl}\cdot\text{OH}$, has $[\text{M}]_{\text{D}} - 41^\circ$, and on treatment of the solution of this chloride with baryta the rotatory power falls to -25° (but no racemisation has occurred since the rotatory power rises again to -41° on the addition of hydrochloric acid). This solution, it is assumed, contains the free base, probably $\text{NMeEtPh}(\text{OH})_2$, which contains a nitrogen atom with only four of the five groups actually different.

There is, however, a difference in character between the two hydroxyl groups, since only one of them behaves as a basic hydroxyl group and is replaceable by an acid radicle.

It is easy to account for the occurrence of optical activity in this compound with the aid of the pyramidal configuration for the nitrogen atom, since if one of the hydroxyl groups is situated at the base of the pyramid and the other at the apex, the arrangement



shown in the figure is obtained, is devoid of a plane of symmetry and therefore capable of giving rise to optical activity.

An optically active compound containing two nitrogen atoms, one of which is asymmetric, $\text{C}_7\text{H}_7\cdot\text{NMePhBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh}$, has been resolved⁸² by crystallisation of the *d*-camphorsulphonate and of the *d*-bromocamphorsulphonate, the salt of the *l*-base is much less soluble than that of the *d*-base in the first case, while the reverse is true for the bromocamphorsulphonate.

The iodide of the *l*-base has $[\text{M}]_{\text{D}} - 411.5^\circ$, and that of the *d*-base has $+403.2^\circ$ in alcohol. Autoracemisation takes place in solution in chloroform and in alcohol, but takes place much more rapidly in the former case than in the latter.

⁸⁰ F. S. Kipping and H. Davies, *Trans.*, 1909, **95**, 69.

⁸¹ J. Meisenheimer, *Ber.*, 1908, **41**, 3966; *A.*, i, 20.

⁸² E. Wedekind and W. Meyer, *ibid.*, 1909, **42**, 303; *A.*, i, 186.

Further instances are recorded of the formation of two compounds, when an asymmetric nitrogen atom is produced in a compound already containing an asymmetric carbon atom.

Thus *l*-menthyl iodoacetate combines with *N*-ethyltetrahydroisoquinoline to give two salts, having $[\alpha]_D -44.9^\circ$ and -17.54° respectively. These give betaines, which become inactive very quickly.⁸³ Similar results have also been obtained with *N*-*n*-propyltetrahydroisoquinoline.⁸⁴

It has also been shown that the addition of an alkyl haloid to an active *N*-alkylated coniine or conhydrine and to 2-phenyl-6-methylpiperidine results in the formation of two stereoisomeric quaternary ammonium salts, but that active alkaloids, coniine excepted, yield only one. Such stereoisomerides were obtained only from piperidine derivatives having a heavy substituent in position 2, and it is concluded that this is necessary in order to give the requisite stability to the group attached to the nitrogen atom.

This view is confirmed by obtaining the active *N*-ethyl- α - and β -pipecolines and forming their additive compounds with benzyl bromide or iodide; from these no isomerides could be separated. Similarly, the additive compound of active amyl iodide and 1-methyl-2-pipecoline seemed to be homogeneous. Therefore a methyl or ethyl group attached to the nitrogen atom and a methyl group in position 2 does not seem to confer the requisite stability on the compound.⁸⁵

This conclusion, however, is not necessary, since it is quite possible, as in the case of the cyanohydrin of mannose, that one of the two possible compounds is formed in very small quantities, and so might be entirely overlooked even after very careful examination had been made. Further, a methyl group was found adequate in the first case of this kind examined, namely, the addition of alkyl iodides to methyl-*d*-amylaniline, in which case two well-characterised isomerides are produced.⁸⁶

In the study of phenyl *p*-tolyl hydrogen phosphate,



some indication has been found that asymmetric derivatives of phosphorus can be resolved into their optically active constituents. The salts of this acid, with eight optically active bases, were examined without any indication being obtained that these salts were mixtures; the melting points and specific rotatory powers of the most and least soluble fractions were in each case found to be

⁸³ E. Wedekind and O. Wedekind, *Ber.*, 1908, **41**, 456; *A.*, 1908, i, 258.

⁸⁴ E. Wedekind and F. Ney, *ibid.*, 1909, **42**, 2138; *A.*, i, 514.

⁸⁵ M. Scholtz, *ibid.*, 1908, **41**, 2005; *A.*, 1908, i, 678.

⁸⁶ H. O. Jones, *Trans.*, 1905, **87**, 135.

⁸⁷ F. S. Kipping and B. D. W. Luff, *ibid.*, 1909, **95**, 1993.

identical. Slight indications that the acid was a mixture were obtained from an examination of the salt with *dl*-hydrindamine, but more definite evidence was obtained when the *d*-hydrindamide was examined. This was separated by fractional crystallisation into two fractions, the less soluble melting at 127° and having $[\alpha]_D - 17.4^\circ$, while the more soluble melts at 82—88° and has $[\alpha]_D - 21.2^\circ$. Similar results were obtained with the *l*-menthylamide. This investigation is being continued, and it seems probable that phosphorus will soon be added to the list of elements which are capable of giving rise to optical activity.

The problem of the isomerism of the cinnamic acids still continues to attract considerable attention, and although several interesting contributions to this subject have appeared, the problem is still far from a satisfactory solution.

It is suggested⁸⁸ that *allocinnamic* acid and the two *isocinnamic* acids are polymorphs. At 105° all three acids are converted into the acid, melting at 42°, and this, when inoculated with the *iso*-cinnamic acid, melting at 58°, or with *allocinnamic* acid, immediately crystallises as a mass of the inoculating acid.

This view is, however, not accepted by E. Erlenmeyer, jun.,⁸⁹ and it has also been shown that a specimen of the *iso*-acid, melting at 58°, was unchanged after keeping for ten or fifteen years in the dark.⁹⁰

A further complication has now been introduced into the problem by the discovery that synthetic cinnamic acid is not a homogeneous substance.⁹¹ By means of fractional crystallisation of the acid, or better by fractional distillation of the ethyl ester, a new acid has been isolated which melts at 128°, has the same molecular formula as cinnamic acid, and therefore is stated to be a new isomeride and is called α -heterocinnamic acid. An amorphous form of this acid is obtained by saponification of the ethyl ester with cold alcoholic potash; this also melts at 128°, but differs from the α -acid in solubility; it is called hetero- β -cinnamic acid, and can be converted into hetero- α -cinnamic acid by repeatedly dissolving it in light petroleum.

It is clear that before the problem of the isomerism of the cinnamic acids can be solved, a careful investigation of the properties of mixtures of the ordinary and *allocinnamic* acids, such as melting point, solubility, and crystalline form, must be carried out. There is at present little or no information on any of these points, and no evidence that the supposed isomerides are not mixed

⁸⁸ E. Biilmann, *Ber.*, 1909, **42**, 182; *A.*, i, 155.

⁸⁹ *Ber.*, 1909, **42**, 521; *A.*, i, 155.

⁹⁰ C. Liebermann, *ibid.*, 1027; *A.*, i, 303.

⁹¹ E. Erlenmeyer, *ibid.*, 502 and 513; *A.*, i, 156.

crystals or even definite molecular compounds, similar to the compound of triphenylmethane and benzene or even to quinhydrone, which may yet give normal values for molecular weight owing to decomposition in solution.

A very large number of isomeric oximes are known, and for the existence of isomeric ketoximes no explanation has been offered except that of stereoisomerism suggested by Hantzsch and Werner. The existence of isomeric aldoximes can be explained on structural grounds, but the existence of isomeric oxygen ethers, such as $C_6H_5 \cdot CH \cdot N \cdot O \cdot C_7H_7$, is definite evidence in favour of the hypothesis of stereoisomerism, although the *N*-substituted aldoximes, $C_6H_5 \cdot CH - N \cdot CH_3$, are very probably derived from the structural



isomeride. Now, although about one hundred and forty of these *N*-substituted aldoximes are known, there is no indication of the existence of isomerides in any but two cases, the methyl derivatives of benzaldoxime and anisaldoxime. These cases have now been re-examined,⁹² and it has been shown in both cases that the supposed isomerides are monohydrated forms of the ordinary *N*-methyl compounds. Consequently, in the case of benzaldoxime, for example, there exist the two oximes, two oxygen ethers (for example, benzyl), and one nitrogen ether.

An examination of the behaviour of the isomeric forms of the oximes of benzaldehyde, of the three nitrobenzaldehydes, and of *p*-triazobenzaldehyde towards diazomethane has shown that the *anti*-aldoximes yield varying amounts, from 6 to 50 per cent., of *O*-methyl ethers, whereas the *syn*-compounds, with one exception, are unchanged.⁹³

The authors are led, therefore, to accept the stereochemical explanation of the isomerism of oximes, although it does not offer a ready explanation of the difference in the behaviour of the *syn*- and *anti*-forms, and suggest a modification of the Hantzsch-Werner hypothesis to account for the stability of the two isomerides.

The view proposed assumes that the carbon atom, doubly linked to the nitrogen atom, exerts some attractive force on the oxygen atom of the hydroxyl group, thus using to some extent the residual valency of the latter. This is represented diagrammatically either as:



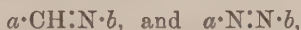
The first method of representation makes the carbon atom

⁹² J. Scheiber, *Annalen*, 1909, **365**, 215; *A.*, i, 391.

⁹³ M. O. Förster and F. P. Dunn, *Trans.*, 1909, **95**, 425.

asymmetric, and is therefore improbable. The second may be regarded favourably on further investigation, since it does in some measure remove the difficulty of accounting for the comparative stability of the two forms.

This view receives support from the fact that among the six types of doubly linked nitrogen compounds:



isomerism has been definitely established in the case of the first four only, and in these the atom, marked with a dot, attached to the nitrogen on the side remote from the double linking is possessed of residual or supplemental valency. It is clear that, in the near future, interesting developments are to be expected in connexion with the Hantzsch-Werner hypothesis of the stereoisomerism of oximes.

H. O. JONES.

ANALYTICAL CHEMISTRY.

THE writer of this report has endeavoured to collate the voluminous literature of this subject so as to form an epitome of the year's work which shall be something more than a mere list or subject-matter index, to show, in fact, the general trend of the investigations in analytical chemistry. He is sensible that many omissions must have been made, but in view of the comprehensive character of the subject, covering as it does the whole range of chemistry, the limit of knowledge of any single reviewer is sufficient excuse for faults of this kind. In the selection of matter the writer has not been guided only by the novelty of the observations, but has taken account of those papers dealing with the revision of existing methods. The somewhat large number of references to the work of past years has been given with the object of completing as far as possible the historical portion of the subject-matter for the guidance of those engaged in research work. The research scheme inaugurated by the Society of Public Analysts and other Analytical Chemists has during the year thoroughly justified its existence, and is responsible for several interesting investigations.

General.

J. Wetzel¹ describes an apparatus for the distillation of mercury. For the purification of mercury, by passing it through a liquid such as dilute nitric acid, an apparatus has been devised by L. J. Desha.² J. H. Hildebrand³ recommends for the same purpose a modification of L. Meyer's method.⁴

A new form of the von Babo-Krafft continuous mercury pump has been devised by C. Hansen.⁵ A safety valve for water pumps, consisting of an automatic cut-off valve to prevent any variation in the water pressure, is described by C. Gerhardt.⁶

¹ *Chem. Zeit.*, 1908, **32**, 1228; *A.*, ii, 145.

² *Amer. Chem. J.*, 1909, **41**, 152; *A.*, ii, 315.

³ *J. Amer. Chem. Soc.*, 1909, **31**, 933; *A.*, ii, 734.

⁴ *Zeitsch. anal. Chem.*, 1863, **2**, 241.

⁵ *Zeitsch. angew. Chem.*, 1909, **22**, 337.

Zeitsch. anal. Chem., 1909, **48**, 460; *A.*, ii, 724.

An ingenious apparatus for the preparation of gases is that devised by M. Gasnier.⁷ It has the advantage over Kipp's apparatus that the pressure remains constant whatever the amount of gas withdrawn. E. E. Reid⁸ describes a gas regulator which is controlled electrically.

R. O. E. Davis⁹ describes a modification of P. A. Kober's apparatus,¹⁰ whereby ammonia may be expelled quantitatively from a liquid by a current of air without distillation. This may prove useful in dealing with liquids having a tendency to froth. The suggestion can be applied to the Kjeldahl method (see also J. Sebelien, A. Brynildsen, and O. Haavardsholm¹¹). A useful bulb-trap for ammonia distillations has been devised by F. Dudy.¹²

H. G. Parker¹³ proposes to perform precipitations in a platinum crucible to the mouth of which is attached a glass tubular portion so that the whole, when fitted together, forms a flask. Subsidence of the precipitate is brought about by centrifuging, and it is washed by syphoning. No estimations are recorded.

W. O. Snelling¹⁴ describes the preparation of platinum felt for use in the Munroe crucible.¹⁵ A list of the precipitates that may be collected in the crucible, and of solvents for the removal of them from the felt, is given by O. D. Swett.¹⁶ A filtering crucible, in which use is made of spongy platinum instead of asbestos, is described by O. Brunck.¹⁷ H. J. F. de Vries¹⁸ puts forward a claim of priority for this crucible, which he has employed in the estimation of potassium.¹⁹ He describes the method of preparing the platinum layer.

L. W. Bosart, jun.,²⁰ recommends a mixture of cotton seed oil (10 parts) and beeswax (1 part) for an oil-bath; the flash point of the mixture is about 300°.

An absorption apparatus, which is a combination of a Volhard's flask with a Winkler's absorption spiral, is described by H. Wölbling.²¹

⁷ *Bull. Soc. chim.*, 1909, [iv], 5, 56; *A.*, ii, 223.

⁸ *Amer. Chem. J.*, 1909, 41, 148; *A.*, ii, 296.

⁹ *J. Amer. Chem. Soc.*, 1909, 31, 556; *A.*, ii, 615.

¹⁰ *Ibid.*, 1908, 30, 1131; *A.*, 1908, ii, 626.

¹¹ *Chem. Zeit.*, 1909, 33, 785; *A.*, ii, 757; F. W. Gill and H. S. Grindley, *ibid.*, 1249; *A.*, ii, 1051.

¹² *Ibid.*, 1158; *A.*, ii, 1050.

¹³ *J. Amer. Chem. Soc.*, 1909, 31, 549; *A.*, ii, 610. ¹⁴ *Ibid.*, 456; *A.*, ii, 431.

¹⁵ *Chem. News*, 1888, 58, 101; *A.*, 1888, 1333.

¹⁶ *J. Amer. Chem. Soc.*, 1909, 31, 928; *A.*, ii, 755.

¹⁷ *Chem. Zeit.*, 1909, 33, 649; *A.*, ii, 826.

¹⁸ *Chem. Weekblad*, 1909 6, 816; *A.*, ii, 1050.

¹⁹ Compare *ibid.*, 1907, 4, 231, 455; 1908, 5, 176, 261; *A.*, 1907, ii, 504, 719; 1908, ii, 430, 534.

²⁰ *J. Amer. Chem. Soc.*, 1909, 31, 724; *A.*, ii, 563.

²¹ *Chem. Zeit.*, 1909, 33, 449.

C. L. Jackson and L. Clarke²² have devised a modification of Scheibler's extraction apparatus.²³ It is suitable for use with large quantities of material.

K. von der Heide²⁴ gives a description of several new forms of percolating and extraction apparatus. An apparatus for extracting plant products with a solvent at its boiling point has been devised by S. J. M. Auld and S. S. Pickles.²⁵ F. Record²⁶ has improved the apparatus previously described²⁷ for extracting a solid and simultaneously filtering the solution obtained. A. H. Fiske²⁸ describes an apparatus for the extraction of liquids with ether. An ingenious condenser for an extraction apparatus is that of C. Fraschina.²⁹ R. Fritsch³⁰ has devised an apparatus which is suitable for extracting liquids with ether or for purifying ether from alcohol.

J. Schroeder³¹ describes an apparatus for determining the solubility of substances at the boiling point of a solvent.

D. D. Gadaskin³² finds that it is advantageous to employ beads of aluminium instead of glass in a dephlegmator column; and several new forms of dephlegmators adapted for liquids of high boiling point are described by M. M. Tichwinsky.³³ P. Malvezin³⁴ has remodelled the Lebel-Henniger column so that it resembles in principle the Coffey still. G. S. Walpole³⁵ has devised a gas-drying apparatus for use with a mechanical pump when conducting distillations under diminished pressure.

J. Lewkowitsch³⁶ gives a description of a new refractometer devised by Harland on the Kohlrausch-Abbe principle, and shows its advantages over other refractometers.

An important paper dealing with the correction of the specific gravity of liquids for the buoyancy of air is that of J. Wade and R. W. Merriman.³⁷

²² *Amer. Chem. J.*, 1909, **42**, 287; *A.*, ii, 826.

²³ *Ber.*, 1880, **13**, 338.

²⁴ *Zeitsch. Nahr. Genussm.*, 1909, **17**, 315; *A.*, ii, 431.

²⁵ *Chem. News*, 1909, **99**, 242; *A.*, ii, 563.

²⁶ *Ibid.*, 53; *A.*, ii, 223.

²⁷ *Ibid.*, 1908, **97**, 280; *A.*, ii, 223.

²⁸ *Amer. Chem. J.*, 1909, **41**, 510; *A.*, ii, 656.

²⁹ *Giorn. Farm. Chim.*, 1909, **58**, 111; *A.*, ii, 564.

³⁰ *Chem. Zeit.*, 1909, **33**, 759; *A.*, i, 547.

³¹ *Zeitsch. anal. Chem.*, 1909, **48**, 349; *A.*, ii, 646.

³² *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 66; *A.*, ii, 378.

³³ *Ibid.*, 81; *A.*, ii, 378.

³⁴ *Bull. Soc. chim.*, 1909, [iv], **5**, 835; *A.* ii, 826.

³⁵ *Proc.*, 1909, **25**, 97.

³⁶ *J. Soc. Chem. Ind.*, 1909, **28**, 77

³⁷ *Trans.*, 1909, **95**, 2174.

Gas Analysis.

J. F. Spencer³⁸ describes a modification of Hempel's gas burette, which obviates the inconvenience of the air space between the burette and the absorbing liquid. A useful volumeter with barometric correction has been devised by Herman.³⁹

G. de Voldere and G. de Smet⁴⁰ describe at length their method of calculating the composition of gas mixtures from data, such as the quantity of oxygen required for complete combustion and the contraction which occurs.⁴¹ For the estimation of carbon monoxide in admixture with methane and hydrogen, V. Nesmjeloff shows⁴² that an accurate method is to pass the gases over copper oxide at 250°.

J. Mai⁴³ proposed the application of Victor Meyer's principle of measuring vapour density to technical gas analysis. In a more recent paper⁴⁴ he has simplified and improved the suggested method. G. von Knorre⁴⁵ proposes a modification of Jager's method⁴⁶ for the estimation of nitrogen in coal gas. After absorbing the carbon dioxide, carbon monoxide, hydrocarbons, and oxygen, the gas is passed to and fro over copper oxide at 250° until no further reduction in volume occurs.

S. H. Davies and B. G. McLellan⁴⁷ describe a modification of Lunge and Zeckendorf's method of estimating carbon dioxide in air, which appears both rapid and accurate. A most important and exhaustive paper is that of W. J. A. Butterfield on the estimation of carbon dioxide and other impurities in air.⁴⁸

The proposal of A. Koepsel⁴⁹ to obtain a continuous register of the composition of a gas mixture by comparing the resistance of a wire suspended in the gas mixture with that of a second wire suspended in air or a gas mixture of constant composition, might probably find practical application.

P. Lemoult⁵⁰ describes the calculation of the calorific power

³⁸ *Ber.*, 1902, **42**, 1786; *A.*, ii, 609.

³⁹ *Bull. Soc. chim. Belg.*, 1908, **22**, 440; *A.*, ii, 181.

⁴⁰ *Bull. Acad. roy. Belg.*, 1909, 622; *A.*, ii, 755.

⁴¹ See also *Rev. gén. Chim. pure et appl.*, 1907, **9**, 395; **10**, 233.

⁴² *Zeitsch. anal. Chem.*, 1909, **48**, 232; *A.*, ii, 519.

⁴³ *Ber.*, 1902, **35**, 4229; *A.*, 1903, ii, 98.

⁴⁴ *Ibid.*, 1908, **41**, 3987; *A.*, ii, 89.

⁴⁵ *Chem. Zeit.*, 1909, **33**, 717; *A.*, ii, 698.

⁴⁶ *J. Gasbeleucht.*, 1898, 764.

⁴⁷ *J. Soc. Chem. Ind.*, 1909, **28**, 232; *A.*, ii, 438.

⁴⁸ *Analyst*, 1909, **34**, 257.

⁴⁹ *Ber. Deutsch. physikal. Ges.*, 1908, 814; 1909, 237; *A.*, ii, 89, 610.

⁵⁰ *Seventh Inter. Cong. Appl. Chem., Analyst*, 1909, **34**, 375.

of combustible gases. J. H. Coste⁵¹ gives some useful data in gas calorimetry obtained with the calorimeters of Junker and Boys.

Inorganic Chemistry.

Qualitative.—In continuation of his work with A. A. Noyes and E. B. Spear,⁵² W. C. Bray⁵³ deals with the separation of the alkali earths and alkalis. E. Ebler⁵⁴ precipitates barium in mixtures with strontium and calcium by addition of concentrated hydrochloric acid. W. A. R. Wilks⁵⁵ makes the interesting observation that one part of sodium can be detected in 50,000 parts of water by the formation of insoluble aluminofluoride on addition of a reagent prepared by dissolving moist alumina and copper acetate in hydrofluoric acid (compare W. C. Ball, p. 146). The reagent does not precipitate potassium or ammonium. According to A. Richaud and Bidot,⁵⁶ the formation of a blue coloration on addition of phosphotungstic acid and alkali to a ferrous salt is a more delicate test than the ferricyanide reaction. A. del Campo⁵⁷ states that 0.005 mg. of zinc in 1 c.c. may be detected by the blue coloration produced on addition of ammonia and resorcinol. P. Lemaire⁵⁸ observes that cadmium and uranium salts give a yellow precipitate on addition of a solution of thiosinamine containing sodium hydroxide. Cadmium only is precipitated by hydrogen sulphide in acid solution, and uranium only by ammonium sulphide. J. H. Pollok⁵⁹ shows by spectrographic analysis that the impurities in commercial thallium are lead, copper, and aluminium. E. Cevoli⁶⁰ states that arsenites (but not arsenates) may be reduced to arsine electrolytically in alkaline solution. P. B. Dallimore⁶¹ has devised a new apparatus for carrying out the Gutzeit test for arsenic. According to Dauvé,⁶² when aluminium foil is immersed in a solution of auric chloride, colloidal gold is produced.⁶³

N. Schoorl has continued his studies on the detection of metallic

⁵¹ *J. Soc. Chem. Ind.*, 1909, **28**, 1231.

⁵² *Ann. Report*, 1908, 181.

⁵³ *Tech. Quart.*, 1908, **21**, 450; *A.*, ii, 431.

⁵⁴ *Zeitsch. anal. Chem.*, 1909, **48**, 175; *A.*, ii, 347.

⁵⁵ *Proc. Camb. Phil. Soc.*, 1909, **15**, 76; *A.*, ii, 618.

⁵⁶ *J. Pharm. Chim.*, 1909, [vi], **29**, 230; *A.*, ii, 350.

⁵⁷ *Anal. Fis. Quim.*, 1909, **7**, 63; *A.*, ii, 439.

⁵⁸ *Ann. Chim. anal.*, 1909, **14**, 6; *A.*, ii, 187.

⁵⁹ *Sci. Proc. Roy. Dubl. Soc.*, 1909, **11**, 338; *A.*, ii, 620.

⁶⁰ *Chem. Zeit.*, 1909, **33**, 1209; *A.*, ii, 1052.

⁶¹ *Pharm. J.*, 1909, [iv], **28**, 324; *A.*, ii, 344.

⁶² *J. Pharm. Chim.*, 1909, [vi], **29**, 241; *A.*, ii, 352.

⁶³ Compare Carnot, *Compt. rend.*, 1883, **97**, 105; *A.*, 1884, 115.

salts microscopically.⁶⁴ M. E. Pozzi-Escot⁶⁵ suggests detecting nickel and cobalt microscopically as dimethylaminobenzene-sulphonates. The same author⁶⁶ describes the reactions of a large number of metals with *p*-sulphobenzeneazodimethylaniline (heli-anthin), and the appearance of the derivatives under the microscope.

E. Covelli⁶⁷ states that "ab rastol" (calcium β -naphthol- α -sulphonate) and concentrated sulphuric acid (formation of red ring) is a delicate test for nitrous acid, and conversely. J. Peset⁶⁸ gives directions for carrying out Mitscherlich's test for phosphorus, and he shows that by its means 0.0085 mg. of phosphorus can be detected with certainty. A method has been devised for the detection of white phosphorus in matches by Sir T. E. Thorpe.⁶⁹ It consists in heating the match or match-composition in a closed bulb containing carbon dioxide at 40—60°. The crystals of white phosphorus which sublime may be distinguished microscopically.

Quantitative.

Indicators.—W. Nernst⁷⁰ has devised a lecture experiment to demonstrate that different indicators exhibit their colour change at different concentrations of hydrogen and hydroxyl ions. When methyl formate is added to a *N*/1000-solution of barium hydroxide at 18°, phenolphthalein is decolorised instantaneously, whilst litmus, cyanine, *p*-nitrophenol, and methyl-orange change respectively after one, fifteen, thirty, and one hundred and twenty minutes. M. Handa⁷¹ points out that the nearer the concentration of hydrogen ions required to produce the colour change in a given indicator is to $10^{-7}N$,⁷² the more delicate is the indicator. He shows that when measured by Nernst's method, above described, methyl-red is slightly less delicate than litmus, and cyanine less delicate than methyl-red. S. P. L. Sørensen⁷³ describes an absolute electro-metric method of estimating the concentration of hydrogen ions, and another method based on the titration of known mixtures of primary and secondary phosphates. The concentration of hydrogen ions in a liquid at the sensitive point of twenty different indicators

⁶⁴ *Ann. Report*, 1908, 183; *Zeitsch. anal. Chem.*, 1909, **48**, 209, 401, 593, 762, 831; *A.*, ii, 521, 762, 831, 938.

⁶⁵ *Ann. Chim. anal.*, 1909, **14**, 207; *A.*, ii, 705.

⁶⁶ *Bull. Soc. chim. Belg.*, 1909, **23**, 299; *A.*, ii, 760.

⁶⁷ *Boll. chim. farm.*, 1909, **48**, 53; *A.*, ii, 452.

⁶⁸ *Zeitsch. anal. Chem.*, 1909, **48**, 35; *A.*, ii, 265.

⁶⁹ *Trans.*, 1909, **95**, 440.

⁷⁰ *Ber.*, 1909, **42**, 3178; *A.*, ii, 878.

⁷¹ *Ibid.*, 3179; *A.*, ii, 931.

⁷² Compare Fels, *Zeitsch. Elektrochem.*, 1904, **10**, 208; *Ann. Report*, 1904, 22.

⁷³ *Biochem. Zeitsch.*, 1909, **21**, 131; *Compt. rend., Carlsberg*, 1909, **8**, 1; *A.*, i, 861.

is given. W. H. Emerson and H. N. Dumas⁷⁴ confirm W. R. Orndorff and J. A. Black's statement⁷⁵ that tetrachlorophenolphthalein is superior to phenolphthalein as an indicator for titrating alcoholic solutions of organic acids. They point out that solutions of stearic and palmitic acids are partly esterified when evaporated with alcohol.

Metals.—F. A. Gooch and R. S. Bosworth⁷⁶ show that silver may be precipitated quantitatively in neutral solution as chromate. The silver chromate filters better if it be dissolved in ammonia and the latter boiled off. Volumetrically the excess of chromate or the silver chromate itself (solution in potassium iodide) may be estimated iodometrically.⁷⁷ Another volumetric method of estimating silver is described by R. S. Bosworth⁷⁸; it consists in titrating with iodine the excess of arsenite required for the reduction of a silver salt. E. Pannain⁷⁹ has devised a new apparatus for determining the end-point when titrating a silver salt by Gay Lussac's method. According to J. M. Wilkie,⁸⁰ lead in presence of a sufficiency of ferric (but not ferrous) iron is completely precipitated by ammonia. For the separation of lead and bismuth, J. C. Galletly and G. G. Henderson⁸¹ recommend Clark's method⁸² with certain modifications for the separation of lead and bismuth. J. J. Fox⁸³ has investigated the solubility of lead sulphate in concentrated solutions of sodium and potassium acetate. In the former case it is found that the solid phase consists of PbSO_4 , whilst in the latter the solubility of the lead sulphate is found to be due to the formation of lead acetate and potassium sulphate, the solid phase consisting of $\text{PbK}_2(\text{SO}_4)_2$, which also results by mixing potassium sulphate with an excess of lead acetate. The same author has shown⁸⁴ that with solutions of ammonium acetate up to a concentration of $3N$, the solid phase consists of lead sulphate, but with more concentrated solution, crystals of the composition $\text{Pb}(\text{NH}_4)_2(\text{SO}_4)_2$ were obtained. B. Oddo and A. Beretta⁸⁵ state that lead may be titrated with potassium chromate, using *s*-diphenylcarbazine as indicator. In another paper⁸⁶ they employ this

⁷⁴ *J. Amer. Chem. Soc.*, 1909, **31**, 949; *A.*, ii, 770.

⁷⁵ *Amer. Chem. J.*, 1909, **41**, 349; *A.*, i, 389.

⁷⁶ *Amer. J. Sci.*, 1909, [iv], **27**, 241; *A.*, ii, 346.

⁷⁷ *Ibid.*, 302; *A.*, ii, 438. ⁷⁸ *Ibid.*, 287; *A.*, ii, 928.

⁷⁹ *Gazzetta*, 1909, **39**, ii, 240; *A.*, ii, 937.

⁸⁰ *J. Soc. Chem. Ind.*, 1909, **28**, 636; *A.*, ii, 703.

⁸¹ *Analyst*, 1909, **34**, 389; *A.*, ii, 833.

⁸² *J. Soc. Chem. Ind.*, 1900, **19**, 26; *A.*, 1900, ii, 371.

⁸³ *Trans.*, 1909, **95**, 878.

⁸⁴ *Proc.*, 1907, **23**, 200.

⁸⁵ *Gazzetta*, 1909, **39**, i, 671; *A.*, ii, 764.

⁸⁶ *Ibid.*, 666; *A.*, ii, 766.

indicator in the titration of mercurous salts with sodium chloride. J. Knox⁸⁷ confirms the accuracy of the method of titrating mercuric salts with thiocyanate devised by Rupp and Krauss,⁸⁸ but he shows that silver cannot be estimated in presence of mercury by the Gay Lussac method as they suggest, because some of the Cl^- ions unite with the Hg^{2+} ions to form undissociated mercuric chloride. Conditions are described, however, whereby the precipitation of silver chloride is complete in presence of mercuric nitrate. H. Wegelius and S. Kilpi⁸⁹ show that prior to precipitation of mercury as sulphide from solutions containing iodides, the latter must be removed by warming with moist silver chloride. In the estimation of copper by liberation of iodine, F. M. Litterscheid⁹⁰ titrates the iodine with arsenious acid. F. A. Gooch and H. L. Ward⁹¹ estimate copper by precipitation as oxalate, and titration of the latter with permanganate. G. Coffetti⁹² describes a method of estimating cuprous oxide in metallic copper by extracting it with ammonia in an atmosphere of hydrogen. A special apparatus is used, which has since been modified by R. H. Greaves,⁹³ who points out that the presence of arsenic, antimony, or iron vitiates the results; antimony and iron are seldom present. He suggests a means of overcoming the error due to arsenic. W. Vaubel⁹⁴ states the conditions of alkalinity under which zinc, copper, and cobalt may be precipitated quantitatively. After investigating several methods for the estimation of antimony and tin, E. Cahen and G. T. Morgan⁹⁵ show that Vortmann and Metzl's method⁹⁶ effects the separation of the two metals, but is only trustworthy for estimating antimony. Czerwek's method, on the other hand,⁹⁷ gives accurate results for the estimation of tin, but not of antimony. With certain modifications, Henz's method⁹⁸—antimony as trisulphide and tin electrolytically—gives accurate results. In separating antimony and tin, L. W. McCay⁹⁹ makes use of the fact that antimony only is precipitated when hydrogen sulphide is passed through a solution to

⁸⁷ *Trans.*, 1909, **95**, 1768.

⁸⁸ *Ber.*, 1902, **35**, 2015; *A.*, 1902, ii, 475.

⁸⁹ *Zeitsch. anorg. Chem.*, 1909, **61**, 413; *A.*, ii, 350.

⁹⁰ *Chem. Zeit.*, 1909, **33**, 263; *A.*, ii, 348.

⁹¹ *Amer. J. Sci.*, 1909, [iv], **27**, 448; *A.*, ii, 703.

⁹² *Gazzetta*, 1909, **39**, i, 137; *A.*, ii, 349.

⁹³ *Chem. News*, 1909, **100**, 233; *A.*, ii, 1054.

⁹⁴ *Zeitsch. angew. Chem.*, 1909, **22**, 1716; *A.*, ii, 832.

⁹⁵ *Analyst*, 1909, **34**, 3; *A.*, ii, 187.

⁹⁶ *Zeitsch. anal. Chem.*, 1905, **44**, 525; *A.*, 1905, ii, 655.

⁹⁷ *Ibid.*, 1906, **45**, 505; *A.*, 1906, ii, 708.

⁹⁸ *Zeitsch. anorg. Chem.*, 1903, **37**, 1; *A.*, 1904, ii, 150.

⁹⁹ *J. Amer. Chem. Soc.*, 1909, **31**, 373; *A.*, ii, 351.

which hydrofluoric acid and sodium acetate have been added. W. Schulte¹ shows that metallic antimony is precipitated from solutions of thioantimonates by aluminium or tin. The latter may be made quantitative. G. Panajotow² shows that antimony sulphide is insoluble in 15 per cent. hydrogen chloride, whilst tin sulphide is soluble. Making use of these facts the two metals may be estimated accurately. K. Meyer³ dissolves the tin in "tin plate" by boiling the latter with sodium peroxide, and weighs the residual iron. When lead and zinc are present they also dissolve, and it is then necessary to estimate the tin by a direct method.

G. Edgar⁴ makes use of the fact that in mixtures with arsenic or antimonious acid, vanadic acid alone is reduced by oxalic or tartaric acid, whereas the three are reduced by sulphurous anhydride, to estimate these acids. J. Knox⁵ points out that the solubility of bismuth trisulphide in alkali sulphides must depend on the formation of a complex anion with the sulphur cation.

In view of the accuracy of the dichromate method, which is practically independent of conditions, it is surprising that so many chemists turn their attention year by year to the titration of ferrous iron by permanganate in the presence of hydrochloric acid. This method can at best be described as empirical, requiring as it does standard conditions for accuracy. But if this be true in the titration of pure ferrous salts, it applies a fortiori in the analysis of ores where constituents of unknown influence are present. The estimation of iron by titration with permanganate in presence of hydrochloric acid has been studied by W. C. Birch,⁶ who finds that Fresenius's method, namely, addition to the solution, after the titration, of a volume of ferrous solution equal to that originally present, retitration, and repetition of this three or four times until a constant reading is obtained, is inaccurate on the evidence which Fresenius himself adduces as well as by his (Birch's) experiments. In a subsequent paper⁷ he recommends metallic copper as a reducing agent for ferric iron. J. A. N. Friend⁸ shows that to ensure accuracy in the hydrochloric acid-permanganate method, the titration must be performed slowly, that a sufficiency of manganous sulphate must be present, and that the dilution of the ferrous

¹ *Metallurgie*, 1909, **6**, 214; *A.*, ii, 522.

² *Ber.*, 1909, **42**, 1296; *A.*, ii, 523.

³ *Zeitsch. angew. Chem.*, 1909, **22**, 68; *A.*, ii, 187.

⁴ *Zeitsch. anorg. Chem.*, 1909, **62**, 77; *A.*, ii, 441.

⁵ *Trans.*, 1909, **95**, 1760.

⁶ *Chem. News*, 1909, **99**, 61, 73; *A.*, ii, 268.

⁷ *Ibid.*, 273; *A.*, ii, 621.

⁸ *Trans.*, 1909, **95**, 1228.

solution should be such as to ensure a good end-point without reducing the accuracy of the titration. The concentration of the hydrogen chloride must not exceed $m/4$. Later he shows⁹ that practically the same precaution must be applied in the estimation of small quantities of ferrous iron by titration with $N/25$ permanganate. G. C. Jones and J. H. Jeffery¹⁰ have determined the conditions in the hydrochloric acid-permanganate method, under which the error in the Reinhardt modification of this method¹¹ is practically negligible, constant, and independent of the amount of iron present.

R. B. Gage¹² points out that the iron in magnetite may be estimated by decomposing the mineral with hydrofluoric acid, and, after adding sufficient calcium fluoride to precipitate the phosphate, titrating with permanganate. J. S. MacLaurin and W. Donovan¹³ show that when iron ores are roasted successively in a current of air and of hydrogen, and dissolved in sulphuric acid, titration with permanganate gives accurate results. Miss E. Hibbert¹⁴ makes use of the reduction of methylene-blue by titanous salts and its non-reduction by ferrous salts as the basis of a method of estimating iron and titanium in mixtures. M. E. Pozzi-Escot¹⁵ describes a method of separating quantitatively iron, aluminium, zinc, and chromium. H. Grossmann¹⁶ has investigated J. A. Sanchez's method of estimating nickel in the presence of cobalt, and condemns it. L. L. de Koninck¹⁷ deals with the precipitation of cobalt as potassium cobaltinitrite. In the separation of nickel and cobalt by the Rosenheim-Huldschinsky method, M. Pritze¹⁸ prefers treatment with dimethylglyoxime to a second shaking with amyl alcohol-ether mixture.

For the gravimetric estimation of magnesium as pyrophosphate, E. Raffa¹⁹ recommends as precipitant an $N/2$ -solution of ammonium disodium phosphate; 0.3 to 0.5 per cent. of magnesium should be present in the liquid, and the precipitate should be washed with 2.5 per cent. ammonia solution. Another series of experiments has been carried out by the same author²⁰ on the precipitation of

⁹ *Proc.*, 1909, **25**, 224.

¹⁰ *Analyst*, 1909, **34**, 306; *A.*, ii, 704. ¹¹ *Chem. Zeit.*, 1889, **13**, 323.

¹² *J. Amer. Chem. Soc.*, 1909, **31**, 381; *A.*, ii, 350.

¹³ *J. Soc. Chem. Ind.*, 1909, **28**, 827; *A.*, ii, 833.

¹⁴ *Ibid.*, 189; *A.*, ii, 351.

¹⁵ *Bull. Soc. chim.*, 1909, [iv], **5**, 558; *A.*, ii, 621.

¹⁶ *Zeitsch. angew. Chem.*, 1909, **22**, 2005; *A.*, ii, 941.

¹⁷ *Bull. Soc. chim. Belg.*, 1909, **23**, 11; *A.*, ii, 269.

¹⁸ *Chem. Zeit.*, 1909, **33**, 694; *A.*, ii, 705.

¹⁹ *Gazzetta*, 1908, **38**, ii, 556; *A.*, ii, 183.

²⁰ *Ibid.*, 1909, **39**, i, 154; *A.*, ii, 347.

magnesium as ammonium magnesium arsenate, but under no conditions are the results as good as those obtained by the phosphate method. F. Hundeshagen²¹ separates calcium from large quantities of magnesium by precipitation as sulphate in presence of alcohol. According to R. Brandenburg,²² the ammonia evolved on boiling cement with a solution of ammonium bromide in absolute alcohol is a measure of the free calcium oxide in cement. W. C. Ball²³ shows that the formation of a yellow precipitate,



when potassium bismuth nitrite containing 1 per cent. of caesium nitrate is added to a sodium salt, is a convenient means of detecting and estimating sodium. A solution of sodium bismuth nitrite may be used for the detection of caesium and rubidium.

W. J. Müller²⁴ estimates thallium by titrating a thallos solution with permanganate or iodine. O. Hauser and F. Wirth²⁵ describe a modification of V. Borelli's method of estimating thorium in monazite sand. V. Borelli has subsequently published another paper on the subject.²⁶ E. Wedekind and S. J. Lewis²⁷ point out that zirconium has not yet been obtained in the pure state, and have devised methods for the estimation of the most commonly occurring impurities. P. E. Browning and H. E. Palmer²⁸ showed that cerium might be estimated in presence of other rare earths by precipitation with an excess of potassium ferricyanide in alkaline solution, the resulting ferrocyanide being titrated with permanganate in the acidified filtrate. In a subsequent paper²⁹ they show that the same principle may be applied for the estimation of thallium. In this case the precipitated thallic hydroxide may also be weighed as Th_2O_3 . F. J. Metzger,³⁰ to estimate cerium in presence of other rare earths, makes use of the fact that cerous sulphate is oxidised to ceric sulphate by bismuthic acid, the excess of the latter being titrated with permanganate. To prevent the precipitation of basic bismuth salts, the presence of ammonium sulphate is necessary.³¹ O. Hauser and F. Wirth³² separate cerium from cerite earths by treating with ammonia and hydrogen peroxide

²¹ *Zeitsch. öffentl. Chem.*, 1909, **15**, 85; *A.*, ii, 438.

²² *Chem. Zeit.*, 1909, **33**, 880; *A.*, ii, 832.

²³ *Trans.*, 1909, **95**, 2126.

²⁴ *Chem. Zeit.*, 1909, **33**, 297; *A.*, ii, 348.

²⁵ *Zeitsch. angew. Chem.*, 1909, **22**, 484; *A.*, ii, 352.

²⁶ *Gazzetta*, 1909, **39**, ii, 425; *A.*, ii, 522.

²⁷ *Trans.*, 1909, **95**, 456.

²⁸ *Zeitsch. anorg. Chem.*, 1908, **59**, 71; *A.*, ii, 736.

²⁹ *Ibid.*, 1909, **62**, 218; *A.*, ii, 620.

³⁰ *J. Amer. Chem. Soc.*, 1909, **31**, 523; *A.*, ii, 620.

³¹ Compare also W. Gibbs, *Amer. Chem. J.*, 1893, **15**, 546; *A.*, 1894, ii, 47; A. Wagner and A. Müller, *Ber.*, 1903, **36**, 282; *A.*, 1903, ii, 242.

³² *Zeitsch. anal. Chem.*, 1909, **48**, 679; *A.*, ii, 940.

and passing a current of chlorine through the liquid in a special form of apparatus. The cerium is weighed as dioxide. G. Edgar³³ describes the iodometric estimation of vanadic, chromic, and ferric oxides in mixtures containing the three. A. W. Gregory³⁴ proposes to estimate vanadium by a tintometric method depending on the change in colour (violet to orange) which takes place on addition of strychnine. Iron interferes, and must be removed previously. P. Jannasch and W. Jilke³⁵ show that phosphoric oxide may be volatilised from the phosphates of iron, chromium, uranium, zinc, nickel, cobalt, and manganese when these are heated in a current of carbon tetrachloride. P. Jannasch and H. F. Harwood³⁶ show that vanadic oxide may also be volatilised similarly. F. J. Metzger and C. E. Taylor³⁷ have devised a method of estimating columbium in presence of tantalum. It consists in adding succinic acid to a solution of the two in concentrated sulphuric acid, when the columbium may be reduced with amalgamated zinc and titrated with permanganate. For the estimation of tantalum, columbium, and titanium, papers by W. B. Giles³⁸ and L. Weiss and M. Landecker³⁹ may be consulted. The paper by the authors last named is a most valuable contribution to the subject. W. E. von John⁴⁰ deals with the estimation of tantalum and columbium. J. P. Lehalleur⁴¹ gives some details for the estimation of molybdenum, vanadium, tungsten, nickel, and chromium. E. Collett and M. Eckardt⁴² review the subject of the estimation of molybdenum in molybdenite, and recommend a method. W. Trautmann⁴³ fuses molybdenite with sodium peroxide under standard conditions, and claims in this way to avoid the solution of certain extraneous metals, besides rendering the estimation more rapid. M. Tschilikin⁴⁴ shows that tungsten may be precipitated quantitatively in acid solution in the cold by means of α -naphthylamine hydrochloride. The composition of the precipitate is



The tungsten is weighed as WO_3 . E. Knecht and Miss E. Hibbert⁴⁵ propose to titrate tungsten dioxide with a ferric salt.

³³ *Amer. J. Sci.*, 1909, [iv], **27**, 174; *A.*, ii, 269.

³⁴ *Proc.*, 1909, **25**, 232.

³⁵ *J. pr. Chem.*, 1909, [ii], **80**, 113; *A.*, ii, 759.

³⁶ *Ibid.*, 127; *A.*, ii, 767.

³⁷ *Zeitsch. anorg. Chem.*, 1909, **62**, 382; *A.*, ii, 702.

³⁸ *Chem. News*, 1909, **99**, 1; *A.*, ii, 352.

³⁹ *Zeitsch. anorg. Chem.*, 1909, **64**, 65; *A.*, ii, 942.

⁴⁰ *Chem. News*, 1909, **100**, 154.

⁴¹ *Mon. Sci.*, 1909, **23**, i, 263; *A.*, ii, 704; compare Jaboulay, *Rev. gén. Chim. pure. Appl.*, 1909, **12**, 142; *A.*, ii, 705.

⁴² *Seventh Inter. Cong. Appl. Chem.*; *Chem. Zeit.*, 1909, **33**, 1968; *A.*, ii, 941

⁴³ *Chem. Zeit.*, 1909, **33**, 1106; *A.*, ii, 942.

⁴⁴ *Ber.*, 1909, **42**, 1302; *A.*, ii, 522.

⁴⁵ *Proc.*, 1909, **25**, 227.

The disappearance of the blue colour due to tungsten pentachloride marks the end of the reaction, or thiocyanate may be used as indicator. According to A. Gutbier and M. Riess,⁴⁶ rhodium may be estimated by precipitating it as metal by hydrazine sulphate.

Non-metals.—The observation of H. Endemann⁴⁷ that the direct titration of hydrogen peroxide with alkali and phenolphthalein indicates only half the acid present has been refuted by O. Lüning.⁴⁸ A. Stähler⁴⁹ proposes to estimate hydroxylamine by reduction to ammonia with an acid solution of a titanous salt. E. Goutal⁵⁰ points out that when steel is dissolved in potassium cupric chloride, occluded gases are given off, and these must be allowed for in the estimation of carbon. A. A. Blair⁵¹ states that under these conditions no hydrocarbons are formed. E. R. Marle⁵² observes that carbonates may be estimated in presence of nitrites by liberating the carbon dioxide by means of potassium dichromate; in presence of sulphides or of sulphites the reaction must be completed by the addition of sulphuric acid owing to the formation of a basic carbonate of chromium. B. Löwinger⁵³ describes a volumetric method of estimating bicarbonates in admixture with normal carbonates.⁵⁴ A. Sanin⁵⁵ proposes to estimate nitrites in presence of nitrates by boiling with a dilute solution of hydroxylamine hydrochloride of known titre towards *N*/20-sodium hydroxide and phenolphthalein, and titrating. A. Hes⁵⁶ deals with the estimation of nitrates by Busch's "nitron" method, especially with the influence of various substances on the results. B. F. Howard and O. Chick⁵⁷ show that nitrates may be estimated gravimetrically as cinchonamine nitrate. According to A. Kleiber,⁵⁸ the whole of the nitrogen in alkali nitrate is obtained as ammonia when a solution is heated with hydrochloric acid, stannous chloride, and iron filings.

In the gravimetric estimation of halogens, E. Alefeld⁵⁹ proposes

⁴⁶ *Ber.*, 1909, **42**, 1427; *A.*, ii, 523.

⁴⁷ *Zeitsch. angew. Chem.*, 1909, **22**, 673; *A.*, ii, 432.

⁴⁸ *Ibid.*, 1549; *A.*, ii, 826.

⁴⁹ *Ber.*, 1909, **42**, 2695; *A.*, ii, 758.

⁵⁰ *Seventh Int. Cong. Appl. Chem.*; *Compt. rend.*, 1909, **148**, 988; *A.*, ii, 519.

⁵¹ *J. Iron and Steel Inst.*, 1909; *A.*, ii, 519.

⁵² *Trans.*, 1909, **95**, 1491.

⁵³ *Chem. Zeit.*, 1909, **33**, 1174; *A.*, ii, 1053.

⁵⁴ Compare E. C. Sutherland, *ibid.*, 1240.

⁵⁵ *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 791; *A.*, ii, 935.

⁵⁶ *Zeitsch. anal. Chem.*, 1909, **48**, 81; *A.*, ii, 265; compare M. Busch, *ibid.*, 368; *A.*, ii, 615; C. Paal and A. Ganghofer, *ibid.*, 545; *A.*, ii, 759; P. Pooth, *ibid.*, 375; *A.*, ii, 615.

⁵⁷ *J. Soc. Chem. Ind.*, 1909, **28**, 53; *A.*, i, 176.

⁵⁸ *Chem. Zeit.*, 1909, **33**, 479; *A.*, ii, 517.

⁵⁹ *Zeitsch. anal. Chem.*, 1909, **48**, 73; *A.*, ii, 262.

to add a small quantity of ether before the addition of silver nitrate. This coagulates the silver halide without heating. V. Rothmund and A. Burgstaller⁶⁰ recommend shaking with ether to coagulate silver halide, and thus prevent it from reacting with silver thiocyanate in Volhard's method. A. Gutbier and F. Falco⁶¹ have modified Frenkel's method⁶² of estimating chlorine in presence of palladium. V. Rothmund⁶³ shows that boiling with titanium sesquisulphate (twice the theoretical quantity) is a convenient means of reducing perchlorates; the excess may then be titrated with a ferric salt. According to A. Stähler,⁶⁴ it is best to estimate the chloride formed. E. Knecht⁶⁵ states, however, that titration with a ferric salt, using thiocyanate as indicator, is quite accurate. To estimate the alkalinity of bleaching powder, K. J. P. Orton and W. J. Jones⁶⁶ add a known excess of *N*/10-hydrochloric acid to a solution, and pass through it in the dark a rapid current of air. When all the chlorine is expelled, the excess of acid is titrated with sodium carbonate and methyl-orange. A useful paper giving the limit of accuracy of three methods of estimating sulphide in alkali cyanide is published by T. Ewan.⁶⁷ J. Milbauer⁶⁸ states conditions whereby sulphites may be titrated accurately with permanganate. A. D. Mitchell and C. Smith⁶⁹ describe a volumetric method for estimating sulphates, which, on the evidence they give, is trustworthy. M. J. van't Kruijs⁷⁰ deals with the conditions necessary to ensure accuracy in the estimation of sulphates as barium sulphate in presence of much calcium salt. G. Kernot⁷¹ draws attention to the solubility of barium sulphate in solution of sodium acetate. H. Grossmann and L. Hölter⁷² show that titration of thiocyanic acid with permanganate gives low results. K. Schröder⁷³ describes conditions whereby accuracy can be attained. H. Pellet⁷⁴ confirms the accuracy of Chesneau's method of estimating phosphorus in iron and steel and of minute quantities

⁶⁰ *Zeitsch. anorg. Chem.*, 1909, **63**, 330; *A.*, ii, 932.

⁶¹ *Zeitsch. anal. Chem.*, 1909, **48**, 555; *A.*, ii, 768.

⁶² *Zeitsch. anorg. Chem.*, 1893, **1**, 217; *A.*, 1893, ii, 195.

⁶³ *Zeitsch. anal. Chem.*, 1909, **62**, 108; *A.*, ii, 434.

⁶⁴ *Chem. Zeit.*, 1909, **33**, 759; *A.*, ii, 699.

⁶⁵ *Proc.*, 1909, **25**, 229.

⁶⁶ *Analyst*, 1909, **34**, 317; *A.*, ii, 701.

⁶⁷ *J. Soc. Chem. Ind.*, 1909, **28**, 10; *A.*, ii, 263.

⁶⁸ *Zeitsch. anal. Chem.*, 1909, **48**, 17; *A.*, ii, 264.

⁶⁹ *Trans.*, 1909, **95**, 2198.

⁷⁰ *Chem. Weekblad*, 1909, **6**, 735; *A.*, ii, 939.

⁷¹ *Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], **15**, 155; *A.*, ii, 940.

⁷² *Chem. Zeit.*, 1909, **33**, 348; *A.*, ii, 449.

⁷³ *Zeitsch. öffentl. Chem.*, 1909, **15**, 321; *A.*, ii, 948; compare also G. Masino,

Chem. Zeit., 1909 **33**, 1173, 1185; *A.*, ii, 1058.

⁷⁴ *Ann. Chim. anal.*, 1908, **14**, 7; *A.*, ii, 182.

of phosphoric acid in general.⁷⁵ Z. Romanski⁷⁶ recommends weighing the molybdic precipitate in the estimation of phosphoric acid in basic slag, and he describes the necessary details. M. Ullmann⁷⁷ proposes a gravimetric molybdate method of estimating phosphoric acid. For the estimation of small quantities of phosphoric acid, I. Pouget and D. Chouchak⁷⁸ make use of the colour (yellow to brown) produced when a solution containing an alkaloid (preferably strychnine) is added to a solution of a phosphate in nitric acid. A. Grete⁷⁹ has improved his method of titrating phosphoric acid with molybdic acid in presence of gelatin⁸⁰ by the employment of an ammoniacal molybdate solution. A. Gutbier and F. Flury⁸¹ show that Frerichs's method of estimating tellurium⁸² gives erroneous results. P. E. Browning and W. R. Flint⁸³ describe a method for the separation of tellurium from selenium.

H. R. Ellis⁸⁴ describes methods for the estimation of cyanamide in sodium cyanamide and "nitrolime." He finds that silver cyanamide has a composition corresponding with $\text{Ag}_2(\text{CN})_2$.

Electrochemical Analysis.—There is nothing of a very novel character to report in this increasingly useful branch of analytical chemistry. T. S. Price and T. C. Humphreys⁸⁵ describe, with the aid of illustrations, various forms of apparatus employed in rapid methods of electro-analysis. Their paper is of value as giving an historical résumé of the subject. A description is given of the estimation of copper and zinc in brass. H. J. S. Sand⁸⁶ has modified his apparatus for the rapid electrolytic separation of metals⁸⁷ so as to render it portable. A. Fischer⁸⁸ describes an arrangement for measuring the cathode potential when using Sand's method.⁸⁹ H. Filippo, jun.,⁹⁰ has devised a modification of Smith's method of rapid electro-analysis,⁹¹ in which a mercury cathode is

⁷⁵ *Ann. Report*, 1908, 187.

⁷⁶ *Chem. Zeit.*, 1909, **33**, 46; *A.*, ii, 182.

⁷⁷ *Seventh Inter. Cong. Appl. Chem.*; *Analyst*, 1909, **34**, 337.

⁷⁸ *Bull. Soc. chim.*, 1909, [iv], **5**, 104; *A.*, ii, 226.

⁷⁹ *Ber.*, 1909, **42**, 3106; *A.*, ii, 936.

⁸⁰ *Ibid.*, 1888, **21**, 2762.

⁸¹ *Chem. News*, 1909, **99**, 217; *A.*, ii, 516.

⁸² *J. pr. Chem.*, 1902, [ii], **66**, 261; *A.*, 1903, ii, 41.

⁸³ *Amer. J. Sci.*, 1909, [iv], **28**, 112; *A.*, ii, 934.

⁸⁴ *Chem. News*, 1909, **100**, 154; *A.*, ii, 1058.

⁸⁵ *J. Soc. Chem. Ind.*, 1909, **28**, 117; *A.*, ii, 342.

⁸⁶ *Chem. Trade J.*, 1909, **45**, 25; *Trans. Faraday Soc.*, 1909, **5**, 159; *A.*, 1910, ii, 66.

⁸⁷ *Ann. Report*, 1908, 194.

⁸⁸ *Chem. Zeit.*, 1909, **33**, 337; *A.*, ii, 521.

⁸⁹ *Trans.*, 1907, **91**, 373; 1908, **93**, 1572.

⁹⁰ *Chem. Weekblad*, 1909, **6**, 226; *A.*, ii, 440.

⁹¹ *J. Amer. Chem. Soc.*, 1903, **25**, 883; 1904, **26**, 1595; 1905, **27**, 1255, 1527; 1907, **29**, 797; *A.*, 1903, ii, 755; 1905, ii, 198, 859; 1906, ii, 194; 1907, ii, 719.

employed. It has the advantage of allowing larger volumes of liquid to be manipulated. W. Böttger⁹² describes an improved method, using a mercury cathode and a helical anode. J. T. Stoddard⁹³ shows that cadmium, copper, nickel, silver, and zinc (and probably other metals) may be precipitated quantitatively from their solutions by *strong* currents in substantially the same time with the use of stationary electrodes as when rotating electrodes are employed. The cathode employed was of platinum-gauze or mercury.⁹⁴ He states that with the exception of silver the character of the deposited metal is scarcely affected by the strength of the current used; it must not exceed 1.5 amperes in the case of silver, otherwise the deposit becomes voluminous and closes the mesh. H. Alders and A. Stähler⁹⁵ deal with the rapid electrolytic separation and estimation of several metals as amalgams. The apparatus consists of a flask having an injecting bottom, through which are sealed three short platinum wires resting externally on a sheet of copper. An annular ring of mercury just covering the platinum points serves as cathode, whilst the anode is a flat coil of platinum-iridium wire capable of rotation. With a current of 3 to 4 amperes at 5 to 6 volts, good results are obtained in the estimation of copper, silver, and mercury as metal. J. W. Turrentine⁹⁶ states that acheson graphite is a satisfactory substitute for platinum in the construction of insoluble electrodes. To render the electrodes non-absorbent they are treated with molten paraffin wax. H. W. Gillett⁹⁷ points out that in a solution of two metals of less potential than hydrogen, the deposition of that of higher potential may be prevented by introducing a metal of intermediate potential even though the voltage used be higher than that of its deposition potential.

F. A. Gooch and F. B. Beyer⁹⁸ have applied their method of simultaneous deposition and filtration⁹⁹ to the estimation of lead and manganese. They show that in the presence of a sufficiency of nitric acid, either metal can be deposited at the cathode as dioxide. H. J. S. Sand¹ describes the estimation of lead electrolytically as dioxide. A. Fischer² states that in the electrolytic precipitation of tin and copper by a method similar to that described by H. J. S.

⁹² *Ber.*, 1909, **42**, 1824; *A.*, ii, 619.

⁹³ *J. Amer. Chem. Soc.*, 1909, **31**, 385; *A.*, ii, 347.

⁹⁴ Compare Cl. Winkler, *Ber.*, 1899, **32**, 2192.

⁹⁵ *Ber.*, 1909, **42**, 2685; *A.*, ii, 764.

⁹⁶ *Seventh Inter. Cong. Appl. Chem.; Analyst*, 1909, **34**, 386.

⁹⁷ *J. Physical. Chem.*, 1909, **13**, 336; *A.*, ii, 521.

⁹⁸ *Amer. J. Sci.*, 1909, [iv], **27**, 59; *A.*, ii, 268.

⁹⁹ *Ann. Report*, 1908, 193. ¹ *Chem. News*, 1909, **100**, 269.

² *Zeitsch. Elektrochem.*, 1909, **15**, 591.

Sand³ for the separation of copper and bismuth, the tin exerts a retarding influence on the copper, necessitating a higher potential. H. J. S. Sand finds, however,⁴ that the copper may be precipitated completely from boiling solutions at an auxiliary potential of 0.60 volt, just as in the absence of tin. C. S. Tatlock⁵ deals with the electrolytic estimation of nickel in ores. C. N. Otin⁶ points out that in the electrolytic estimation of manganese by Engel's method⁷ the deposit formed at the anode contains 7 per cent. of metallic manganese, which may, however, be prevented by lowering the current density at the cathode or by adding ammonium sulphate (2 grams per 100 c.c.). It then has the composition of manganese dioxide after drying at 200—220°. Addition of alcohol causes the deposit to adhere to the anode.

Employing a rotating silver anode and a mercury cathode, J. S. Goldbaum and E. F. Smith⁸ have succeeded in estimating barium or strontium in admixture with calcium with a fair degree of accuracy by taking advantage of their respective deposition potentials. The halogen may be estimated from the increase in weight of the anode. For the electrolytic estimation of thallium, G. W. Morden⁹ advises the use of a very dilute zinc-cadmium amalgam instead of pure mercury as cathode in conjunction with a rotating anode.

Water Analysis.

For the estimation of dissolved oxygen in water, G. B. Frankforter, G. W. Walker, and A. D. Wilhoit¹⁰ show that the colorimetric ammoniacal cuprous chloride method of Sir W. Ramsay and Miss I. Homfray¹¹ gives accurate results if precautions are taken to prevent the oxidation of the cuprous solution. They have constructed an apparatus for the purpose entirely of glass. W. P. Jorissen¹² finds in support of the statement of W. P. Jorissen and W. E. Ringer¹³ that for the estimation of dissolved oxygen in sea water, G. Romijn's method¹⁴ gives low results.

The determination of the hardness of water by the soap method

³ *Trans.*, 1907, **91**, 395.

⁴ *Proc.*, 1909, **25**, 228.

⁵ *Zeitsch. anal. Chem.*, 1909, **48**, 433; *A.*, ii, 766.

⁶ *Zeitsch. Elektrochem.*, 1909, **15**, 385 and 386; *A.*, ii, 703.

⁷ *Ber.*, 1895, **28**, 3182; *A.*, 1896, ii, 276; *Zeitsch. Elektrochem.*, 1897, **3**, 286, 305; *A.*, 1898, ii, 52.

⁸ *J. Amer. Chem. Soc.*, 1909, **31**, 900; *A.*, ii, 763.

⁹ *Ibid.*, 1045; *A.*, ii, 1054.

¹⁰ *Ibid.*, 35; *A.*, ii, 263.

¹¹ *J. Soc. Chem. Ind.*, 1901, **20**, 1071; *A.*, 1902, ii, 171.

¹² *Chem. Weekblad*, 1909, **6**, 123; *A.*, ii, 343.

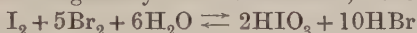
¹³ *Ibid.*, 1906, **2**, 781; *A.*, 1906, ii, 490.

¹⁴ *Rec. trav. Chim.*, 1893, **12**, 241; 1896, **15**, 76; *A.*, 1894, ii, 28; 1896, ii, 579.

has practically been superseded by acidimetric and alkalimetric methods, but some useful data are given by G. Piccinini.¹⁵

L. Farcy¹⁶ points out that the methods of estimating nitrates devised by G. McGowan¹⁷ and by G. Frerichs¹⁸ are inaccurate in presence of ammonium salts. During the year several authors have referred to the well-known fact that Grandval and Lajoux's phenol-sulphonic acid method of estimating nitrates is inaccurate in the presence of halides, and no reference need be made to these papers. An important paper on the subject has been published, however, by E. M. Chamot and D. S. Pratt,¹⁹ who bring forward evidence that the yellow colour produced in the cold is due to the nitration of phenol-2:4-disulphonic acid, the compound formed being the alkali derivative of a nitrophenolsulphonic acid. The authors are still investigating the method, which has long needed placing on a sound scientific basis.

According to S. Bugarszky and B. Horvath,²⁰ the reaction



is practically complete from left to right in presence of excess of bromine, which may be boiled off without reversing the reaction. If, after this, potassium iodide be added, the liberated iodine may be titrated. It is stated to be a good method for the estimation of iodine in waters in presence of chlorides, bromides, ammonium salts, nitrates, and nitrites.

Organic Chemistry.

Qualitative.

There are a number of observations calling for notice in this department. A. Vorisek²¹ shows that methyl alcohol may be detected readily in admixture with ethyl alcohol by distilling 0.5 to 1.0 c.c. of the mixture with 0.8 per cent. chromic acid and 4 to 5 c.c. of water. The distillate is then tested for formaldehyde. In this way 0.001 gram of methyl alcohol can be detected in 1 c.c. of ethyl alcohol. G. B. Neave²² has confirmed the Sabatier-Senderens catalytic test for distinguishing between primary, secondary, and tertiary alcohols.²³

¹⁵ *Atti R. Accad. Sci. Torino*, 1909, **44**, 842; *A.*, ii, 832.

¹⁶ *Bull. Soc. chim.*, 1909, [iv], **5**, 775; *A.*, ii, 758.

¹⁷ *Trans.*, 1891, **59**, 530.

¹⁸ *Arch. Pharm.*, 1903, **241**, 47; *A.*, 1903, ii, 328.

¹⁹ *J. Amer. Chem. Soc.*, 1909, **31**, 922; *A.*, i, 641.

²⁰ *Zeitsch. anorg. Chem.*, 1909, **63**, 184; *A.*, ii, 932.

²¹ *J. Soc. Chem. Ind.*, 1909, **28**, 823; *A.*, ii, 834.

²² *Analyst*, 1909, **34**, 346; *A.*, ii, 835.

²³ *Ann. Report*, 1905, 194.

G. Denigès has published a series of papers on certain colour reactions. He states²⁴ that in the resorcinol test for tartaric acid, the chromophore is $\text{HO}\cdot\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}\cdot\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}\cdot\text{OH}$ and that the colour reaction varies in intensity according to the nature of the groups united to the free affinities. He gives directions for distinguishing between glyceric, tartaric, and tartronic acids. Later²⁵ he shows that the mechanism of the reaction consists in the formation of aldehydes from these compounds, which aldehydes condense with the resorcinol or other phenol to form coloured derivatives. He describes some colour reactions with certain phenols and opium alkaloids in presence of sulphuric acid,²⁶ whilst in a still later paper²⁷ he shows that these reactions are due to methylglyoxal, and that they can be obtained with the oxidation products of other polyhydroxy-alcohols besides glycerol. In a further communication,²⁸ he shows that methylglyoxal in presence of sulphuric acid gives colour reactions with numerous organic substances. These reactions may be made use of conversely as a test for glycerol.²⁹ Lactic acid yields acetaldehyde, and glycollic acid, formaldehyde, when the respective acids are warmed with sulphuric acid, and colour reactions characteristic of these aldehydes may be applied for the detection of the acids.³⁰ It is shown³¹ that allyl alcohol may be detected by the colour reactions of its oxidation (by bromine) products—glycer-aldehyde and dihydroxyacetone—with certain alkaloids and sulphuric acid.

Dealing with the detection of various substances in foods, etc., a few papers may be referred to. E. Covelli³² describes several colour reactions for the detection of "abrostol" (calcium- β -naphthol- α -sulphonate). The reaction with nitrous acid is referred to on p. 141. O. Carletti³³ describes a delicate colour reaction (with sulphuric acid and alcoholic tartaric acid) for the detection of "abrostol." Pyrogallol gives the same reaction.³⁴ A. Labat³⁵ describes colour reactions of hydrastine, hydrastinine, and narcotine when these are heated with sulphuric acid and certain phenols. Oxidation of the alkaloids mentioned with permanganate produces opianic acid, colour reactions of which with sulphuric acid and

²⁴ *Bull. Soc. chim.*, 1909, [iv], 5, 19; *A.*, ii, 80.

²⁵ *Ibid.*, 353; *A.*, i, 378.

²⁶ *Compt. rend.*, 1909, 148, 172, 282; *A.*, ii, 272, 273.

²⁷ *Ibid.*, 422; *A.*, ii, 448.

²⁸ *Bull. Soc. chim.*, 1909, [iv], 5, 649; *A.*, ii, 624.

²⁹ *Compt. rend.*, 1909, 148, 570; *A.*, ii, 353.

³⁰ *Bull. Soc. chim.*, 1909, [iv], 5, 647; *A.*, ii, 627.

³¹ *Ibid.*, 878; *A.*, ii, 944.

³² *Boll. chim. farm.*, 1909, 48, 53; *A.*, ii, 452.

³³ *Ibid.*, 1906, 6, 223; *A.*, ii, 528.

³⁴ *Ibid.*, 441; *A.*, ii, 769.

³⁵ *Bull. Soc. chim.*, 1909, [iv], 5, 742, 743; *A.*, ii, 710.

phenols are described. Several colour reactions for the detection of aniline are given by J. Peset.³⁶ The detection of methylaniline and dimethylaniline in mixtures of the two is dealt with by H. Emde.³⁷ Mlle. A. Jonescu³⁸ states that hydrogen peroxide converts benzoic acid as well as "saccharin"³⁹ into salicylic acid, which may then be detected by the well-known colour reaction with ferric chloride.⁴⁰ The fact that iodine combines with tannin has been utilised by C. Conti⁴¹ for the detection of coal-tar colours in wines. The natural colouring matters of wine are precipitated on addition of iodine, but not artificial colours.

J. Gnezda⁴² describes some colour reactions of the sugars with indole derivatives. J. Ville and E. Derrien⁴³ show that Pettenkofer's reactions for sucrose and Seliwanoff's reaction for ketoses are due to the formation of 2-hydroxy-4-methylfurfuraldehyde.

S. Fränkel and R. Allers⁴⁴ state that adrenaline, when warmed with iodic acid, gives a red coloration, believed to be an iodoso-derivative. To detect adrenaline in blood or extracts of organs, etc., G. Comessatti⁴⁵ centrifuges with mercuric chloride and alcohol, when, after standing for twelve to twenty-four hours, if adrenaline is present, a red colour appears in the supernatant liquid. K. Boas⁴⁶ succeeded in obtaining the reaction only when the mixture was heated. The colour reactions of adrenaline and of catechol with ferric chloride and of adrenaline with iodic acid and dichromate are, according to G. Bayer,⁴⁷ rendered more sensitive in presence of certain aromatic aminosulphonic acids. Certain products of the putrefaction of flesh increase the delicacy of the iodine reaction; it was this fact which led Abelous, Soulie, and Toujan⁴⁸ to the belief that the adrenaline increases when putrid meat is added to minced adrenal gland. Colour reactions of nevraltetine, pyramidone, and antipyrine are described by A. Monferrino.⁴⁹ O. Hammarsten⁵⁰ describes a colour reaction of cholic acid with hydrochloric acid.

³⁶ *Zeitsch. anal. Chem.*, 1909, **48**, 37; *A.*, ii, 274.

³⁷ *Arch. Pharm.*, 1909, **247**, 77; *A.*, ii, 275.

³⁸ *J. Pharm. Chim.*, 1909, [vi], **29**, 523; *A.*, ii, 627.

³⁹ See Leys, *Compt. rend.*, 1901, **132**, 1056; *A.*, 1901, ii, 488.

⁴⁰ Compare *J. Pharm. Chim.*, 1909, [vi], **30**, 16; *A.*, ii, 707.

⁴¹ *Boll. chim. farm.*, 1909, **48**, 295; *A.*, ii, 711.

⁴² *Compt. rend.*, 1909, **148**, 485; *A.*, ii, 451.

⁴³ *Bull. Soc. chim.*, 1909, [iv], **5**, 895; *A.*, ii, 946.

⁴⁴ *Biochem. Zeitsch.*, 1909, **18**, 40; *A.*, ii, 628.

⁴⁵ *Berl. Klin. Woch.*, 1909, **46**, 8; *A.*, ii, 628.

⁴⁶ *Zentr. Physiol.*, 1909, **22**, 825; *A.*, ii, 628.

⁴⁷ *Biochem. Zeitsch.*, 1909, **20**, 178; *A.*, ii, 839.

⁴⁸ *Compt. rend. Soc. Biol.*, 1905, **57**, 301, 589.

⁴⁹ *Boll. chim. farm.*, 1909, **48**, 515; *A.*, ii, 838.

⁵⁰ *Zeitsch. physiol. Chem.*, 1909, **61**, 495; *A.*, ii, 836.

For the detection of peptolytic enzymes of the erepsin type, E. Abderhalden and A. Schittenhelm⁵¹ suggest treating an alkaline solution of glycyl-*L*-tyrosine ("Peptone Roche") with the suspected extract. A positive result is indicated by the separation of tyrosine.

Quantitative.

Ultimate Analysis.—A convenient apparatus for indicating the rate of a current of oxygen in the estimation of carbon by combustion is described by M. Dennstedt.⁵² M. Delépine⁵³ has devised a boat for containing a substance undergoing combustion, which appears to have some advantages over the ordinary form. B. Blount and A. G. Levy⁵⁴ give their experience in the use of quartz combustion tubes. Their experiments, although confined to the estimation of carbon in steel, are suggestive for organic analysis. J. A. Fries⁵⁵ describes a bomb calorimeter for the determination of the heat of combustion or for the estimation of carbon. Hydrogen may also be estimated if the bomb be lined with platinum. A. Kleine⁵⁶ has devised a modification of the Corleis flask for the estimation of carbon by the wet process, and also an improved form of soda-lime tube. E. Berl and A. G. Innes⁵⁷ describe conditions whereby carbon in such substances as cellulose may be estimated accurately by the wet process. M. E. Pozzi-Escot⁵⁸ describes a modification of the Von Koneck nickel crucible for organic analysis by fusion with sodium peroxide. C. W. Bacon⁵⁹ has investigated Stepanoff's method of estimating halogens in organic compounds.⁶⁰ He finds that as originally described the method gives inaccurate results, and he has therefore modified it, but the modification he proposes leaves nothing to be desired on the score of accuracy. For the estimation of arsenic in organic compounds, H. V. Little, E. Cahen, and G. T. Morgan⁶¹ ignite with sodium peroxide, reduce with hydriodic acid, and titrate with iodine and starch in presence of disodium hydrogen phosphate.

Estimation of Compounds and Determination of Constants.—The method described by J. J. Sudborough and H. Hibbert⁶² for the

⁵¹ *Zitsch. physiol. Chem.*, 1909, **61**, 421; *A.*, ii, 840.

⁵² *Chem. Zeit.*, 1909, **33**, 769; *A.*, ii, 759.

⁵³ *Bull. Soc. chim.*, 1909, [iv], **5**, 876; *A.*, ii, 937.

⁵⁴ *Analyst*, 1909, **34**, 88; *A.*, ii, 346.

⁵⁵ *J. Amer. Chem. Soc.*, 1909, **31**, 272; *A.*, ii, 270.

⁵⁶ *Chem. Zeit.*, 1909, **33**, 376; *A.*, ii, 437.

⁵⁷ *Ber.*, 1909, **42**, 1305; *A.*, ii, 520.

⁵⁸ *Ann. Chim. anal.*, 1909, **14**, 5; *A.*, ii, 188.

⁵⁹ *Chem. News*, 1909, **99**, 6; *A.*, ii, 179.

⁶⁰ *Ann. Report*, 1906, 212.

⁶¹ *Trans.*, 1909, **95**, 1477,

⁶² *Proc.*, 1904, **20**, 165.

estimation of amines is now found by the same chemists⁶³ to be applicable generally for the estimation of primary and secondary amines, and of mixtures of these with tertiary amines. According to Dreger,⁶⁴ diphenylamine may be estimated by precipitation as the tetrabromo-derivative (m. p. 102°) by adding bromine to an alcoholic solution. A. Casolari⁶⁵ titrates quinol with iodine and starch in presence of sodium hydrogen carbonate. J. C. Irvine⁶⁶ shows that the specific rotatory power of chitin, determined in hydrochloric acid (D 1.16), is $[\alpha]_D - 14.1^\circ$ ($c = 1.75$). This value, although calculated on the chitin itself, is in reality due to the hydrochloride; on allowing the solution to stand, the specific rotatory power changes to that of glucosamine hydrochloride, $[\alpha]_D + 56^\circ$. V. H. Veley⁶⁷ finds that the affinity values of a few alkaloids—those derived from opium—are less than $1 \cdot 10^{-7}$, the values of the greater number being between this and $3 \cdot 10^{-5}$ (the value of ammonia), whilst a few (for example, brucine, spartine, and cotarine) give higher values, and hence must be classed with the tetra-alkylammonium hydroxides. B. F. Howard and O. Chick⁶⁸ have redetermined the specific rotatory powers in alcoholic solution of cinchonamine, cinchonidine, concuscomine, cupreine, and quinine. Unfortunately, the concentrations of the solutions are not given. They have also determined the molecular weights and the number of methoxyl groups in these alkaloids. In the estimation of nicotine, G. Bertrand and M. Javillier⁶⁹ propose to isolate the base by precipitation as silicotungstate. P. A. Levene and D. D. van Slyke⁷⁰ describe methods for the separation and estimation of leucine, *d*-isoleucine, and *d*-valine in the products of the hydrolysis of proteins.

Commercial Products: Food and Drugs.—Instead of distilling off the ammonia formed in the Kjeldahl process, H. G. Bennett⁷¹ recommends titrating the neutralised liquid after addition of formaldehyde with standard alkali. A method for the estimation of small quantities of nitrogen in soils, etc., was devised by E. A. Mitscherlich in 1907, and has been modified by him and his co-workers, P. Herz, E. Merres, and D. J. Hissink.⁷² In broad

⁶³ *Trans.*, 1909, **95**, 477.

⁶⁴ *Zeitsch. Schiess. Sprengstoffw.*, 1909, **4**, 123; *A.*, ii, 708.

⁶⁵ *Gazzetta*, 1909, **39**, i, 589; *A.*, ii, 769.

⁶⁶ *Trans.*, 1909, **95**, 564.

⁶⁷ *Ibid.*, 758.

⁶⁸ *J. Soc. Chem. Ind.*, 1909, **28**, 54; *A.*, i, 176.

⁶⁹ *Bull. Soc. chim.*, 1909, [iv], **5**, 241; *A.*, ii, 450.

⁷⁰ *J. Biol. Chem.*, 1909, **6**, 391, 419; *A.*, ii, 947.

⁷¹ *J. Soc. Chem. Ind.*, 1909, **28**, 291; *A.*, ii, 436; compare Ronchèse, *Ann Report*, 1907, 201.

⁷² See *Landw. Jahrb.*, 1909, **22**, 631; *Landw. Versuchs-Stat.*, 1909, **70**, 405; *Chem. Weekblad*, 1909, **6**, 2229; *A.*, ii, 436, 614.

outline the latest modification of the method is to distil the substance with Devada's alloy and sodium hydroxide, whereby the inorganic nitrogen is converted into ammonia. The organic nitrogen is then converted on Kjeldahl's lines. V. Schenke⁷³ prefers, when large quantities of nitrates are present, treating first with potassium chlorate and sulphuric acid, and then with "reduced iron." E. A. Mitscherlich⁷⁴ cites experiments showing that Schenke's method is inaccurate for nitrous nitrogen.⁷⁵

For the estimation of reducing sugars, P. Maillard⁷⁶ recommends Bonnan's volumetric method.⁷⁷ According to the evidence brought forward, it lacks the accuracy of the Fehling method in its most recent form, and could only be applied in the case of small quantities of reducing sugars; it has been used chiefly in clinical practice. F. M. Litterscheid and J. Bornemann⁷⁸ propose to determine the copper reduced by dextrose iodometrically (compare Litterscheid, p. 143). A somewhat similar proposal is made for reducing sugars generally by E. Rupp and F. Lehmann.⁷⁹ L. Eynon⁸⁰ shows that the influence of clarification with basic lead acetate in the analysis of sugar products is greater on the direct polarimetric reading than on the Clerget value. The influence is chiefly due to the precipitation of lævulose by basic lead acetate.⁸¹ In harmony with Eynon's results is the observation of the writer and G. McLaren,⁸² that the Clerget value of molasses agrees, as a rule, well with the percentage of sucrose determined by the copper method. The writer, in conjunction with L. Eynon and J. H. Lane,⁸³ has redetermined the solution densities of dextrose, lævulose, and maltose. These three sugars were specially prepared in a high degree of purity for the purpose. The specific rotatory powers of the preparations were as follows: Dextrose, $[\alpha]_D^{17} + 52.72^\circ$ ($c=10$); lævulose, $[\alpha]_D^{18.5} - 93.83^\circ$ ($c=10$); maltose $[\alpha]_D^{17.5} + 137.72^\circ$ ($c=5.7$). A Jägerschmid's resorcinol method of detecting caramel in wine, spirits, etc.,⁸⁴ is, according to W. Bremer and F. Sponnagel,⁸⁵ capable of detecting added invert-sugar in natural honey.

Among the papers published during the year on the estimation of starch, L. T. Thorne and E. H. Jeffers⁸⁶ describe a modification

⁷³ *Chem. Zeit.*, 1909, **33**, 712; *A.*, ii, 699. ⁷⁴ *Ibid.*, 1058; *A.*, ii, 935.

⁷⁵ Compare, however, Schenke, *ibid.*, 203; *A.*, ii, 1051.

⁷⁶ *Ann. Chim. anal.*, 1909, **14**, 342; *A.*, ii, 945.

⁷⁷ Compare A. J. Salm, *Chem. Weekblad*, 1903, **1**, 12.

⁷⁸ *Zeitsch. angew. Chem.*, 1909, **22**, 2423; *A.*, 1910, ii, 80.

⁷⁹ *Arch. Pharm.*, 1909, **247**, 516.

⁸⁰ *Seventh Inter. Cong. Appl. Chem.*; *Analyst*, 1909, **34**, 349.

⁸¹ Compare A. H. Bryan, *Zeitsch. Ver. deut. Zuckerind.*, 1909, **1**; *A.*, ii, 271.

⁸² *Loc. cit.*, 350.

⁸³ *Ibid.*, 351.

⁸⁴ *Zeitsch. Nahr. Genussm.*, 1909, **17**, 269.

⁸⁵ *Ibid.*, 664.

⁸⁶ *Seventh Inter. Cong. Appl. Chem.*; *Analyst*, 1909, **34**, 332.

of Lintner's method.⁸⁷ M. Buisson⁸⁸ proposes to estimate starch polarimetrically after heating for forty-five minutes with picric acid solution.

In a useful and comprehensive paper, A. Smetham⁸⁹ gives the proximate composition of a number of new imported feeding stuffs used as cattle food, as well as of products produced in this country. He draws attention to the great utility of the Soja bean, and the paper may be consulted for analyses of these.⁹⁰ The fact that certain beans (*Phaseolus lunatus*) imported from Java contain a cyanogenetic glucoside and an enzyme capable of splitting off hydrogen cyanide when they are steeped, has long been known.⁹¹ Smetham again calls attention to this fact,⁹² and also to a similar danger in the case of some kinds of manioc.

F. C. Cook⁹³ deals with Jaffe's colorimetric estimation of creatinine. A. C. Chapman⁹⁴ has placed this method on a much sounder basis, by showing that the various colour changes are due to reduction of picric acid by creatinine, successively to a dinitro-monaminophenol (probably the 2:4:6-derivative), mononitrodi-aminophenol (picramic acid), and triaminophenol.

P. Malvezin⁹⁵ describes conditions of extracting wines with ether, whereby the partition of the volatile acids in that solvent is constant.⁹⁶ K. von der Heide and H. Steiner have published two useful papers on the estimation of succinic acid and of malic acid in wine.⁹⁷ G. Perrin⁹⁸ points out that inositol is a constituent of natural wines. He was, however, anticipated by Meillère,⁹⁹ who criticises his method.¹

A paper on the methods of examining vinegar is published by J. Brode and W. Lange.² Although of a preliminary nature only, the paper is useful in indicating the degree of accuracy of several methods.

⁸⁷ *Ann. Report*, 1908, 202.

⁸⁸ *Seventh Inter. Cong. Appl. Chem.*; *J. Soc. Chem. Ind.*, 1909, **28**, 806.

⁸⁹ *J. Roy. Lancashire Agric. Soc.*, 1909.

⁹⁰ Compare also *U.S. Depart. Agric. Bull.*, October, 1909; *Bull. Imp. Inst.*, 1909, **7**, 308.

⁹¹ *Ann. Report*, 1906, 286.

⁹² Compare also A. Barillé, *J. Pharm. Chim.*, 1909, **29**, 422.

⁹³ *J. Amer. Chem. Soc.*, 1909, **31**, 673; *A.*, ii, 709.

⁹⁴ *Analyst*, 1909, **34**, 475; *A.*, ii, 948.

⁹⁵ *Compt. rend.*, 1909, **148**, 784; *A.*, ii, 444.

⁹⁶ Compare N. Gallo, *Staz. sper. agrar. Ital.*, 1909, **42**, 37; *A.*, ii, 524.

⁹⁷ *Zeitsch. Nahr. Genussm.*, 1909, **17**, 291, 307; *A.*, ii, 444, 445.

⁹⁸ *Ann. Chim. anal.*, 1909, **14**, 182; *A.*, ii, 624.

⁹⁹ *J. Pharm. Chim.*, 1908, [vi], **28**, 289.

¹ *Ibid.*, 1909, [vi], **30**, 247; *A.*, ii, 945.

² *Arb. Kais. Gesund. Amt.*, 1909, **30**, 1; *A.*, ii, 356.

In the analysis of brewing materials, H. van Laer³ has modified his method of measuring the catalytic power of malt, making it much more rapid, whilst A. C. Chapman⁴ has further improved his cinchonine method of estimating hop tannin. W. M. Gardner and H. H. Hodgson⁵ describe an iodometric method of estimating phenolic substances, including the tannins. E. F. Harrison⁶ deals with the diastatic power of malt extract. He recommends the method described in the British Pharmaceutical Codex, 1907, page 402, which was devised by himself and Gair. The method disregards Kjeldahl's law of proportionality, in addition to which no evidence is adduced that the amount of starch converted under the conditions given is proportional to the diastatic power of the malt extract.

O. Weber⁷ describes a method of estimating formic acid in fruit juices. F. Auerbach and W. Plüddemann⁸ show that formic acid may be estimated volumetrically by taking advantage of its reducing action towards mercuric chloride, whilst H. Franzen and G. Greve⁹ deal with the same principle applied gravimetrically.

H. D. Richmond's annual report on the composition of milk¹⁰ gives the average composition of 17,433 authentic samples. H. S. Shrewsbury and A. W. Knapp¹¹ describe a colorimetric method of estimating formaldehyde in milk. H. Rosset,¹² for the estimation of fluorides in foods, introduces the barium precipitate into a leaden vessel, and heats with sulphuric acid, holding a glass dish above the fumes. He compares the degree of etching with standards, and thus claims to make the method quantitative.

For the determination of the hydrogen value in unsaturated compounds,¹³ S. Fokin¹⁴ has devised a new apparatus. A. H. Bennett¹⁵ shows that in Walther's method of determining citral in lemon oil¹⁶ it is advantageous to use alcoholic sodium or potassium hydroxide instead of sodium hydrogen carbonate.¹⁷ Useful physical data for the analysis of lemon, bergamot, and

³ *J. Inst. Brewing*, 1909, **15**, 553.

⁴ *Ibid.*, 360.

⁵ *Seventh Inter. Cong. Appl. Chem.*; *Analyst*, 1909, **34**, 371; *Trans.*, 1909, **95**, 1819.

⁶ *Pharm. J.*, 1909, [iv], **26**, 388.

⁷ *Zeitsch. Nahr. Genussm.*, 1909, **17**, 194; *A.*, ii, 355.

⁸ *Arb. Kais. Gesund. Amt*, 1909, **30**, 178; *A.*, ii, 355.

⁹ *J. pr. Chem.*, 1909, [ii], **80**, 368; *A.*, ii, 1057.

¹⁰ *Analyst*, 1909, **34**, 208.

¹¹ *Ibid.*, 12; *A.*, ii, 192.

¹² *Ann. Chim. anal.*, 1909, **14**, 365; *A.*, ii, 933.

¹³ *Ann. Report*, 1903, 202.

¹⁴ *Zeitsch. anal. Chem.*, 1909, **48**, 337.

¹⁵ *Analyst*, 1909, **34**, 14; *A.*, ii, 192.

¹⁶ *Pharm. Zentr.-h.*, 1899, **40**, 621; *A.*, 1900, ii, 173.

¹⁷ Compare Schimmel & Co., *Reports*, April, 1900.

orange oils are given by E. Berté and Romeo.¹⁸ R. A. Cripps and J. A. Brown¹⁹ propose to determine moisture in spices by measuring the acetylene produced by contact with calcium carbide.²⁰ The difference between this and the total volatile matter gives the essential oil.

T. R. Hodgson²¹ finds that Lasserre's method of separating volatile fatty acids²² gives results of approximate accuracy, whilst a similar conclusion is arrived at quite independently by C. A. Keane and P. Narracott.²³ Continuing his experiments,²⁴ R. K. Dons²⁵ has determined the solubility in hot water and the volatility of some of the fatty acids occurring in butter fat. A most interesting piece of work has been carried out by K. S. Caldwell and W. H. Hurtley.²⁶ They have distilled butter fat, cocoanut oil, and their fatty acids in a cathode light vacuum. The temperatures of distillation differed widely from those stated by F. Krafft and H. Weilandt,²⁷ and the conclusion is arrived at that under these conditions a liquid has no boiling point.

As usual, a large number of papers have appeared dealing with the analysis of fats and oils, and of these a few will be referred to. H. Bull and J. C. F. Johannesen²⁸ describe a modification of Hehner and Mitchell's bromine addition gravimetric method of differentiating fish oils. M. Tortelli²⁹ shows that the Maumené thermal value of fats and oils is constant for one and the same substance. He has restandardised the method, and gives values for several fats and oils. R. R. Tatlock and R. T. Thomson³⁰ have made a useful study of the Polenske test in the analysis of fats and oils (insoluble volatile acids), and they find it scarcely capable of detecting 10 per cent. of cocoanut oil in butter, whilst it appears trustworthy within limits of 5 per cent. for estimating cocoanut oil in margarine. L. Laband³¹ finds the method uncertain for butter, but trustworthy for the detection of beef fat in lard.

C. Paal and C. Amberger³² have published a most important

¹⁸ *Chemist and Druggist*, 1909, 74; *A.*, ii, 352.

¹⁹ *Analyst*, 1909, **34**, 519.

²⁰ P. V. Dupré, *ibid.*, 1906, **31**, 213.

²¹ *Analyst*, 1909, **34**, 435; *A.*, ii, 947.

²² *Ann. Inst. Pasteur*, 1907, **21**, 829; *A.*, 1907, ii, 991.

²³ *Analyst*, 1909, **34**, 436; *A.*, ii, 947.

²⁴ *Ann. Report*, 1908, 203.

²⁵ *Zeitsch. Nahr. Genussm.*, 1908, **16**, 705; *A.*, ii, 190.

²⁶ *Trans.*, 1909, **95**, 853. ²⁷ *Ber.*, 1896, **29**, 1316.

²⁸ *Chem. Zeit.*, 1909, **33**, 73; *A.*, ii, 274.

²⁹ *Ibid.*, 125, 184, 171, 184.

³⁰ *J. Soc. Chem. Ind.*, 1909, **28**, 69.

³¹ *Zeitsch. Nahr. Genussm.*, 1909, **18**, 289.

³² *Ibid.*, 1909, **17**, 1.

paper on the metallic salts of the volatile fatty acids present in butter fat and in cocoanut oil, and the detection of cocoanut oil in butter. M. Monhaupt³³ has modified the Reichert-Meissl and Kirschner processes, and shows that small quantities of butter fat may be detected in much cotton seed oil. I. Klimont and E. Meisels³⁴ point out that the fats of the goose and duck contain, like those of other domestic animals, mixed glycerides.

K. Lendrich and E. Nottbohm³⁵ have elaborated an accurate method of estimating caffeine in coffee. L. E. Walbum³⁶ has modified Baudin's method of estimating cantharidin³⁷ so that the results are more in accord with the more accurate method of Self and Greenish.³⁸ W. Lohmann³⁹ deals with the distinctions between natural and synthetic camphor; the optical inactivity of the synthetic product and the presence of certain impurities are the means suggested. E. Deussen⁴⁰ describes methods for the estimation of camphor in spirit of camphor. H. C. Wood, jun.,⁴¹ has devised a method for the assay of ergot; it depends on the estimation of the "resin."

A method for the estimation of combined sulphur in caoutchouc is described by T. Budde.⁴²

Synthetic indigo may contain bromoindigotins, and A. Binz and T. Marx⁴³ show that when extracted with chloroform the tribromo-derivative is dissolved; a mixture of glacial acetic acid (80 vols.) and concentrated sulphuric acid (20 vols.) dissolves indigotin and bromoindigotin, but not the dibromo-derivative.

Toxicological Analysis.

Of the few papers classed under this head, the following appear worthy of notice. In carrying out Gasparini's electrolytic method of destroying organic matter prior to testing for mineral poisons, M. Miorandi⁴⁴ points out that it is advantageous to use carbon electrodes instead of platinum, and ammonium persulphate instead of nitric acid. The detection of minute quantities of mercury in

³³ *Chem. Zeit.*, 1909, **33**, 305.

³⁴ *Monatsh.*, 1909, **30**, 341; *A.*, ii, 597.

³⁵ *Zeitsch. Nahr. Genussm.*, 1909, **17**, 241; *A.*, ii, 449.

³⁶ *Pharm. Zentr.-h.*, 1909, **50**, 661; *A.*, ii, 839.

³⁷ *J. Pharm. Chim.*, 1888, **18**, 391.

³⁸ *Pharm. J.*, 1907, [iv], **24**, 324.

³⁹ *Ber.*, 1909, **19**, 222; *A.*, ii, 525.

⁴⁰ *Arch. Pharm.*, 1909, **247**, 307; *A.*, ii, 770.

⁴¹ *Amer. J. Pharm.*, 1909, **81**, 215.

⁴² *Gummi-Zeit.*, 1909, **23**, 1143; *A.*, ii, 828.

⁴³ *Zeitsch. angew. Chem.*, 1909, **22**, 1757; *A.*, ii, 839.

⁴⁴ *Gazzetta*, 1909, **39**, i, 175; *A.*, ii, 342.

urine, stomach contents, etc., is dealt with by C. Lombardo⁴⁵ and by C. Stich.⁴⁶

C. Reichard,⁴⁷ in dealing with the detection of morphine, points out that that alkaloid is partly converted into dehydromorphine in the animal body. W. J. Dilling⁴⁸ summarises the reactions of coniine, conhydrine, α -conhydrine, γ -coniceine, and of the trimethylpiperidine isomeric with coniine discovered by I. Guareschi.⁴⁹ In another paper⁵⁰ he deals with the isolation of conium alkaloids from animal tissues. G. Candussio⁵¹ and U. Saporetti⁵² show how α - and β -eucaine can be distinguished by their reactions with bromine and iodine.⁵³

Physiological.

A very important paper on the isolation and estimation of glycogen is published by E. Pflüger.⁵⁴ It is shown that animal glycogen is not attacked by hot alkalis, and is best isolated by boiling a given organ with 30 per cent. potassium hydroxide.

F. W. Gill and H. S. Grindley⁵⁵ show by comparing the results of estimations of total sulphur in urine by O. Folin's sodium peroxide method⁵⁶ with those obtained by the nitric acid method, that the former are low. O. Folin⁵⁷ states that his precise directions have not been followed; and E. Abderhalden and C. Funk⁵⁸ assert that the sodium peroxide method gives good results. They point out⁵⁹ that Modrakowski⁶⁰ used sodium peroxide for the purpose.⁶¹

A. Florence⁶² recommends removing uric acid and creatinine by precipitation with basic lead acetate before estimating urea in urine by the hypobromite method. Modifications of the hypobromite method of estimating urea are described by F. Haesler⁶³ and by

⁴⁵ *Arch. Farm. speriment.*, 1909, **7**, 400; *A.*, ii, 185.

⁴⁶ *Pharm. Zeit.*, 1909, **54**, 833; *A.*, ii, 1055.

⁴⁷ *Pharm. Zentr.-h.*, 1908, **49**, 951; *A.*, ii, 194.

⁴⁸ *Pharm. J.*, 1909, [iv], **29**, 34 *et seq.*; *A.*, ii, 771.

⁴⁹ *Atti R. Accad. Sci. Torino*, 1908, **43**, 1095; *A.*, 1908, i, 1008.

⁵⁰ *Biochem. J.*, 1909, **4**, 286; *A.*, ii, 709.

⁵¹ *Boil. chim. farm.*, 1909, **48**, 95; *A.*, ii, 450.

⁵² *Ibid.*, 479; *A.*, ii, 771.

⁵³ Compare *ibid.*, 630; *A.*, ii, 838.

⁵⁴ *Pflüger's Archiv*, 1909, **129**, 362; *A.*, ii, 947.

⁵⁵ *J. Amer. Chem. Soc.*, 1909, **31**, 52; *A.*, ii, 263.

⁵⁶ *J. Biol. Chem.*, 1906, **1**, 131; *A.*, 1906, ii, 123.

⁵⁷ *J. Amer. Chem. Soc.*, 1909, **31**, 284; *A.*, ii, 263.

⁵⁸ *Zeitsch. physiol. Chem.*, 1909, **58**, 331; *A.*, ii, 263.

⁵⁹ *Ibid.*, **59**, 121; *A.*, ii, 343.

⁶⁰ *Ibid.*, 1903, **38**, 362.

⁶¹ See also S. R. Benedict, *J. Biol. Chem.*, 1909, **6**, 363; *A.*, ii, 827; S. Ritson, *Biochem. J.*, 1909, **4**, 337; *A.*, ii, 827.

⁶² *Compt. rend.*, 1909, **148**, 943; *A.*, ii, 449.

⁶³ *Chem. Zeit.*, 1909, **33**, 110; *A.*, ii, 275.

A. Jolles.⁶⁴ R. F. Bacon,⁶⁵ for the rapid estimation of urea in urine, makes use of the facts (a) that urea yields nitrogen and carbon dioxide on treatment with Millon's reagent, whereas ammonia is unaffected, and (b) that both urea and ammonia yield nitrogen when treated with alkaline hypobromite.

For the estimation of glycuronic acid in urine, C. Tollens⁶⁶ precipitates with ammonia, distils the precipitate with hydrochloric acid, and estimates the furfuraldehyde in the distillate as phloroglucide. The same observer shows that the naphtha-resorcinol colour reaction⁶⁷ may also be used as the basis of an approximately quantitative method.

M. Nishi⁶⁸ states that quinine may be estimated in urine by rendering the liquid alkaline, extracting with ether, and precipitating as quinine hydrogen citrate by addition of citric acid.

ARTHUR R. LING.

⁶⁴ *Zeitsch. anal. Chem.*, 1909, **48**, 26; *A.*, ii, 275.

⁶⁵ *Philippine J. Sci.*, 1909, **4**, 153; *A.*, ii, 757.

⁶⁶ *Zeitsch. physiol. Chem.*, 1909, **61**, 95; *A.*, ii, 836; compare *Ber.*, 1907, **40** 4513; *A.*, 1908, ii, 74.

⁶⁷ *Ann. Report*, 1908, 199.

⁶⁸ *Arch. exp. Path. Pharm.*, 1909, **60**, 312; *A.*, ii, 710.

PHYSIOLOGICAL CHEMISTRY.

IN last year's report I alluded to the issue of two important series of monographs on biochemical subjects; during the last twelve months these have continued to appear. One of these is Carl Oppenheimer's *Handbuch der Biochemie*; it was intended originally to complete this work in twenty fasciculi, but that number has already been exceeded, and there is no sign at present that the supply is exhausted. The other series is that of the Biochemical Monographs, which is under the editorship of Drs. F. G. Hopkins and R. H. Aders Plimmer. Two more of these have been issued, one by Dr. S. B. Schryver on the General Characters of the Proteins, and the second by Dr. Thomas B. Osborne on the Vegetable Proteins, which supplies a long-felt gap in chemical literature. In both series the subject-matter is up to date, and one's only regret, looking to the rapid acquisition of new knowledge, is how soon much that has been written with infinite patience and care will become ancient history. One more new book is worthy of mention, and that is a practical handbook,¹ which resembles Oppenheimer's in being written by numerous authors; Emil Abderhalden is its editor, and it will quickly find a place in the library of every well-equipped laboratory and researcher.

The year has been notable for the holding in London of the Congress of Applied Chemistry, and this event will long live in the memory of all who attended it. At the final meeting the position of Physiological Chemistry was vindicated, and in future it will be a separate section, instead of, as heretofore, a sub-section of Organic Chemistry. Our section (or sub-section, as it then was) was well attended, and one had the opportunity of making the personal acquaintance of workers from all parts of the globe, and of hearing them speak. Where so many important and interesting papers were read, it seems invidious to select a few for special mention; the parts of the programme which, however, appeared to me as specially interesting were (1) the series of practical demonstrations which were given in the new Institute of Physiology at University College; (2) the able presentment of their views on

¹ *Handbuch der biochemischen Arbeitsmethoden.*

alcoholic fermentation by Drs. Harden and Young; (3) the interesting paper by Dr. Steudel on uric acid, to which I shall have to refer later; and (4) the important group of communications on the lipoids, which were introduced by a lucid exposition of his views by Professor Hans Meyer, one of the pioneers who first recognised the physiological importance of these substances.

In the selection of papers for more extended review, I find, on looking up the year's literature, not only the *embarras des richesses* to which I also referred last year, but this year I find a special difficulty in my task, for no new note has been struck, no great discovery made, and the subjects treated are so varied and numerous that connecting threads are hard to weave. A number of small and disjointed details are to hand, none of them of vast importance, and at first I thought my report would dwindle down to making an abstract of the physiological abstracts, which would not be much more than a catalogue of them. If this report ultimately possesses this character, which I always endeavour to avoid, the reader must attribute it more to the material at my disposal than to any fault of my own. There is an increasing tendency in some quarters to publish researches piecemeal, and dribblets of what really may be an important piece of work issue month by month, and one's attention and interest vanish, and the sequence of the story is lost, much as it is when one reads a novel issued in a monthly magazine. One can quite understand, in these strenuous days, the value of a preliminary communication in order to ensure priority, but that is a very different thing to what I am alluding to; it really looks as if some workers are seeking fame rather by the number of papers to which their name is attached than by making solid and sure progress by taking a little more time over their work, and finally presenting it in more or less complete form.

Having, however, delivered myself of this protest, let us now proceed to consider the work of the year; and in so doing I shall endeavour to select subjects of general and practical interest.

Proteins.

The work on protein synthesis does not appear, so far as one can judge from published papers, any further advanced than it was some years ago when Emil Fischer first applied himself to the problem. Abderhalden and his colleagues are more concerned at present with protein cleavage, and this is no doubt the right method of work; correct analysis must necessarily precede synthesis. It is much to be regretted that Abderhalden is not free from reproach in reference to what one may term the "dribblet" method of publication, for he exhibits not only remarkable industry, but, unlike many mere

slaves to work, he possesses ideas. One excellent specimen of a new idea is seen in the new method he has introduced of partial hydrolysis; the distinction between proteins will probably be found to rest not only in the kind and amount of the final cleavage products so much as in the way in which the individual amino-acids are linked together. For this purpose, partial hydrolysis, with a resulting yield of polypeptides, is of great utility. In his first attempt in this direction,² polypeptides were separated from the partial hydrolysis of edestin, elastin, and keratin. One of these contained glutamic acid and tryptophan, another the same two substances with leucine in addition, and a third, tyrosine, glycine, and leucine. From keratin a polypeptide containing cystine, glutamic acid, and tyrosine, and another containing histidine and leucine were separated; and from elastin, *l*-leucyl-*d*-alanine and *d*-alanyl-*l*-leucine were obtained.

In a later paper,³ which is one of a large number relating to the composition of different silks (see forthcoming index), he obtained, by what he terms a lucky accident, glycyl-*l*-tyrosine directly from the products of the partial hydrolysis of silk. The hydrolysis had been carried out with 70 per cent. sulphuric acid at room temperature. Similarly, two dipeptides, one of them leucyl-glycine, and the other probably glycyl-leucine, were obtained from elastin.

The onlookers at the progress of our knowledge of protein chemistry, which had its inception in Emil Fischer's remarkable work, cannot but feel that the method of partial hydrolysis is fraught with importance, and would desire that the method be worked out more thoroughly. Our feelings of satisfaction that one of the most difficult of biochemical questions is on the way to solution must, however, have received a set-back on reading a paper from the versatile pen of the veteran worker and thinker, Eduard Pflüger,⁴ whose opinions are entitled to the deepest respect. Pflüger, it is true, has, or had, a theory of protein constitution, and so is not altogether unbiassed; his views on the work of Fischer, Abderhalden, and their disciples are decidedly pessimistic. He doubts whether all this gigantic array of experiments brings us any nearer to a solution of the question of protein constitution. He certainly points out that in their work a large portion of the molecule is still unaccounted for; and no one can deny that in the case of the more complex proteins the cleavage products obtained do not account for much more than half the original

² *Zeitsch. physiol. Chem.*, 1909, **58**, 373; *A.*, i, 273.

³ *Ibid.*, 1909, **62**, 415; *A.*, i, 859.

⁴ *Pflüger's Archiv*, 1909, **129**, 99; *A.*, i, 685.

molecule. Perhaps half is better than none, but the remaining half will undoubtedly be the more difficult one to tackle. Pflüger adopts as the only certain test for a protein its capacity to maintain life and enter into the composition of protoplasm; if this definition is accepted, gelatin, protamines (many of which are poisonous), proteoses, and polypeptides must be excluded from the protein family. This definition strikes one as too narrow, and too biological; it is quite possible that members of a group may possess chemical characters in common which justify the use of a common general name, and yet they may have a very different physiological action. This is admitted for substances of which the chemical constitution is known, and it is no great stretch of the imagination to conceive the same to be true of substances which, like the proteins, are still in chemical darkness.

Whatever may turn out to be the ultimate value of such analytical work, it is certainly of minor value unless it is correct; and biochemists no doubt received another shock when a recent paper by Levene and van Slyke⁵ appeared. These careful workers showed that all previous methods employed for the isolation and estimation of the leucine fraction, and for the separation of its constituents (leucine, *isoleucine*, and valine), were incorrect, and that by new and trustworthy methods the figures obtained differ enormously from those given by Abderhalden. Abderhalden's work in this direction has, of course, not been useless, but now it only fulfils the humble rôle of showing subsequent workers how not to do it: our knowledge of the proteins is thus delayed, for all the laborious analyses of the leucine fraction (and possibly of other fractions, too) will have to be repeated.

Purine Metabolism.

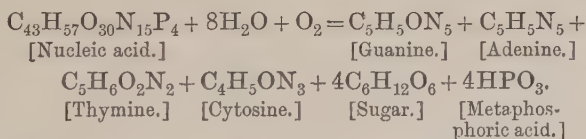
The general view now held with regard to the origin of purine substances in the urine is that in mammals they arise from the catabolism and oxidation of the main constituent of the nuclei of cells, which is called nucleic acid. Within recent years doubts have arisen whether this statement contains the whole truth, and also whether the theory which has been largely deduced from experiments on animals can be applied without reserve to man. It is naturally from the human point of view that the question derives its main importance, and all that we can learn about the origin and fate of uric acid is of great practical interest. Many human ills have been attributed in the past to excess of uric acid, and some enthusiasts are inclined to regard it as the source of all our woes. Without accepting such a sweeping belief, the fact remains that this waste product is by no means harmless. In man, no doubt, the

⁵ *J. Biol. Chem.*, 1909, 6, 391, 419, *A.*, ii, 947,

question is complicated by his varied diet, and some of the purine substances, which in health there seems no difficulty in getting rid of, are introduced with the food, and are of purely exogenous origin; thus meat contains a considerable amount of hypoxanthine, and tea and coffee account for the methylated purine derivatives of the urine (M. Krüger).⁶ This factor is, however, fully recognised by experimenters, and observations on man are always made on a purine-free diet if one seeks to investigate the more important question of the endogenous origin of purine.

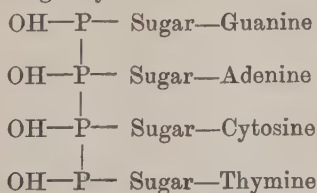
Before, however, we can proceed to a systematic review of the point at issue, it will be necessary to allude briefly to the constitution of nucleic acid, and the prevailing views regarding its decomposition in the body.

Nucleic Acid.—Since the work of I. Bang and Walter Jones (described in last year's Report), it has been recognised that there are two principal kinds of nucleic acid. One of these, now termed guanylic acid, yields, on decomposition, three products only, namely, guanine, phosphoric acid, and a pentose. The other, which may be termed nucleic acid proper, is apparently more widely distributed, and more abundant in cells generally. At the recent Congress, to which allusion has already been made, Steudel gave the results of his careful analyses, and proposed an empirical formula for it which differs somewhat from that advocated by Schmiedeberg last year. The following equation indicates what it is, as well as the way it splits up on decomposition with water and oxygen:



That is to say, the cleavage products are two amino-purine bases (guanine and adenine), two pyrimidine bases (thymine and cytosine), four molecules of a sugar of the hexose family, but not yet fully identified, and four molecules of metaphosphoric acid.

He also put forward tentatively his view regarding the constitution of the nucleic acid molecule, which may be represented roughly in the following way:



⁶ *Biochem. Zeitsch.*, 1909, 15, 361; *A.*, ii, 166.

That is, we have a chain of four atoms of phosphorus, each of which is united on the one side to a hydroxyl group, and on the other to a hexose molecule; each hexose group is further united to a base, and thus the four bases enumerated above are attached to the molecule.

It is impossible to prophesy whether such a formula will stand the tests of criticism and renewed experiment, but, at any rate, we have a working hypothesis, and one can only hope that if we have not reached the last chapter in an interesting series of researches which was initiated by Miescher many years ago, we must be somewhat near the penultimate one.

The view now held with regard to the decomposition of this complex molecule in metabolic processes within the body is briefly as follows. The decomposition is accomplished by certain tissue enzymes, which have been studied in extracts of tissues and organs; their distribution varies a good deal both in different animals and in their different organs, but, speaking generally, they are most abundant in the liver and spleen. The first to act is called *nuclease*; it liberates from nucleic acid its purine bases. The next to come into play are called deamidising enzymes, because they remove the amino-group; one of them, *adenase*, converts adenine into hypoxanthine (mono-oxypurine); the other, called *guanase*, converts guanine into xanthine (dioxypurine); finally, *oxydases* step in which transform hypoxanthine into xanthine, and xanthine into uric acid (trioxypurine). But even that does not bring the long list to a conclusion, for in certain organs (for example, the liver) there is a capacity to destroy the uric acid after it is formed, and so we are normally protected from a too great accumulation of this substance. What exactly happens to the uric acid is uncertain, although it is supposed that the products of breakdown are less harmful than uric acid itself. The enzyme responsible for uric acid destruction is called the *uricolytic* enzyme. The uric acid which ultimately escapes in the urine is the undestroyed residue; the urine, however, contains a certain amount of the purine bases which have not been converted into uric acid.

This view renders it easy to understand how too great an action of uric acid-forming enzymes and too little activity of the uric acid-destroying enzyme may lead to a pathological condition in which uric acid accumulates in the body. To those who have read my previous reports, this will be an old story, but I have thought it best to recapitulate the main data of the theory in order to pave the way to what now follows.

What we have now to consider are the weak points in the theory, for renewed experiments have shown that it is quite possible that

(1) purines may arise otherwise than from the cleavage of nucleic acid, and (2) that in man the uricolytic ferment is absent from extracts of his tissues and organs; if this is really the case, man is inferior to most other mammals in his capacity to deal with one of his enemies.

Leathes⁷ was the first to point out that uric acid excretion is related in some way to muscular exercise; it is, for instance, more abundantly eliminated during the day than during the night. Kennaway's⁸ more recent work confirms this view. Walter Jones (working with Leonard⁹), who, of course, on such a question speaks with authority, takes it as established that muscular exercise contributes to uric acid formation. Muscle, however, is admittedly poor in nucleic acid, although, as is well known, it is rich in hypoxanthine; it therefore appears that not only may muscle or flesh, when used as food, increase the purine compounds in the urine exogenously, but, in a similar way, the hypoxanthine present may form the source of a true endogenous production of uric acid. The hypoxanthine in muscle may be spoken of as "preformed," and its origin is not directly connected with nuclein metabolism at all, since it occurs in the absence of adenase, an essential factor in the passage from nucleic acid to hypoxanthine.

Aders Plimmer¹⁰ gives details of a metabolism experiment on a healthy man which casts considerable doubt on the whole theory. The subject of the experiment was fed on a meat diet, on a purine-free diet, and a purine-rich diet; also, on certain days, guanine and xanthine were added to the diet. Scarcely any relation between the purines given and the purines (including uric acid) found in the urine was discoverable; he therefore considers that the prevalent opinion that the purines of the food and tissues are the *sole* source of uric acid needs revision. If we italicise the word *sole*, most physiologists will probably agree with him, although I am doubtful whether many will accept without more cogent proof his alternative theory that leucocytes in the manner of invertebrate animals excrete uric acid in some mysterious way without reference to the metabolism of their nuclei.

The Uricolytic Enzyme.—Most interest and much work has centred around this interesting enzyme. Its presence has been determined with certainty in the majority of animals in which it has been looked for, and is usually most abundant in the liver, although it may be present in other organs, such as the kidney. We

⁷ *J. Physiol.*, 1906, **35**, 125, 205; *A.*, 1907, ii, 114, 376.

⁸ *Ibid.*, 1908, **38**, 1; *A.*, ii, 166.

⁹ *J. Biol. Chem.*, 1909, **6**, 453; *A.*, ii, 911.

¹⁰ *J. Physiol.*, 1909, **39**, 98; *A.*, ii, 817.

may take first some of the most recent experiments that support this view. Wiechowski,¹¹ for instance, working with the surviving liver and kidney of dogs, finds that these organs decompose uric acid entirely, and that allantoin is one of the products of its decomposition, although probably not an abundant one, for the urine contains mere traces. He¹² admits, however, that if uricolysis occurs at all in human tissues, the action is extremely small as compared with that in other animals.

The uricolytic action, when present, appears to be reversible, or, at any rate, counteracted by other enzymes; the latter view appears to be that adopted by a group of Italian workers.¹³ A dog's liver was perfused with arterial blood containing uric acid, and it was found that a marked decrease of the uric acid took place; but by perfusing the same liver with blood saturated with carbon dioxide, the uric acid, which had disappeared, appears again: the enzyme to which the restoration is due is stated to occur in the blood and blood-serum, but not in the blood-free liver. They then added to finely-minced surviving liver a large number of the decomposition products of uric acid, but usually no formation of uric acid occurred; the only positive result was obtained by the addition of dialuric acid and urea.

The question of uric acid destruction has also been taken up by Battelli and Stern.¹⁴ They regard it as a complex process, and the appearance of allantoin only one of many possibilities; and the enzyme which oxidises uric acid to allantoin is named by them *uricase*. Its action is most energetic in free oxygen, but, in many tissues, inhibiting substances delay its action. Uricase is absent in birds, which is what one would anticipate; it is also absent in man. The absence of uricolysis in man is also noted by Wells and Corper,¹⁵ and by W. Jones and Miller.¹⁶ Jones and Miller started their work by searching for the uricolytic enzyme in human tissues from cases of gout. They found it absent, but this cannot be the cause of that disease, for they then found, in confirmation of Wiechowski, that the same is true for normal human organs. They found also that another member of the uric acid group of enzymes is also

¹¹ *Arch. exp. Path. Pharm.*, 1909, **60**, 185; *A.*, ii, 329.

¹² *Biochem. Zeitsch.*, 1909, **19**, 368; *A.*, ii, 749.

¹³ Ascoli and Izar, *Zeitsch. physiol. Chem.*, 1909, **58**, 529; *A.*, ii, 329; *ibid.*, 1909, **62**, 347; *A.*, ii, 909; Bezzola, Izar, and Preti, *ibid.*, 1909, **62**, 229, 354; *A.*, ii, 1909.

¹⁴ *Biochem. Zeitsch.*, 1909, **19**, 219; *A.*, ii, 749.

¹⁵ *J. Biol. Chem.*, 1909, **6**, 321; *A.*, ii, 749; *ibid.*, **6**, 469; *A.*, ii, 1034. These observers deal specially with foetal tissues.

¹⁶ *Zeitsch. physiol. Chem.*, 1909, **61**, 395; *A.*, ii, 821; see also W. Jones and Winternitz *ibid.*, 1909, **60**, 180; *A.*, ii, 594.

absent, namely, adenase, and this contrasts with the pig, in which animal, guanase is absent. In man the principal seat of uric acid formation (from guanine) is the liver, but guanase is also present to some extent in the lung and kidney, although absent from the spleen.

Differences were previously known to exist between different animals in the presence and distribution of the enzymes which lead to the formation of uric acid, so the absence of adenase in man is not remarkably noteworthy; the puzzling and at present inexplicable fact is the absence of the uricolytic enzyme in human tissues. From the evolutionary point of view, its development would naturally be regarded as an important asset in the struggle for existence. Can it be that a further development still has taken place in man, and that so little uric acid is normally produced that there is no necessity to destroy it? I do not feel in the least inclined to answer this question in the affirmative, and it is impossible to be certain what is the solution of the problem until more work casts more light upon it.

A Schittenhelm's¹⁷ views on the matter are, however, very suggestive, and will make physiologists pause before they regard the action of organ-extracts as a complete picture of actual metabolism in the body. It is quite true that the extracts of human tissues contain no uricolytic enzyme, and often no adenase, but it is unscientific and unwise to conclude, from such results obtained post-mortem, that metabolism runs a similar negative course during life. In fact, the metabolism experiments he has performed indicate that adenine is converted into hypoxanthine, and that the uric acid formed is in part destroyed (reappearing mainly as urea) in human beings.

Enzymes.

The specific action of enzymes is one of their most interesting properties, and Emil Fischer's well-known "lock and key" hypothesis furnishes a ready explanation for the specificity; there must be some relationship, for instance, between the configuration of the enzyme maltase and the sugar maltose on which it acts, that enables it to unlock from their union the two molecules of hexose of which maltose is composed; on the other hand, an absence of such related configuration renders this enzyme inoperative even on such closely related sugars as sucrose and lactose.

There is no doubt that the various members of the large protein family differ from each other a good deal more than do the three disaccharides just mentioned; nevertheless, from the point of view of their susceptibility to enzymic cleavage, there is a closer simi-

¹⁷ *Zeitsch. physiol. Chem.*, 1909, 63, 248; *A.*, 1910, ii, 52.

larity, as has been recently pointed out in a thoughtful essay on the Proteins by T. Brailsford Robertson.¹⁸ All true proteins and a large number of polypeptides are hydrolysable by trypsin, and the great majority of them by pepsin also.

The general trend of present day work on the enzymes is to emphasise specificity, and to seek for the agents responsible for the cleavage of comparatively simple substances. The discovery by Kossel and Dakin a few years ago of arginase, an enzyme capable of hydrolytically cleaving arginine and nothing else, was the starting point of this line of research. The discovery of creatase and creatinase, mentioned in last year's report, is an instance of the same sort of work. This year we have to add to the list, and to chronicle the identification of *salikase*, which hydrolyses salicin to dextrose and saliginin, and of *arbutase*, which hydrolyses arbutin into quinol and dextrose.¹⁹ A glance through our monthly abstracts will show how numerous are the papers relating to another group of enzymes, namely, the oxydases, and it will be sufficient to say in reference to this work that specificity seems as evident there as in enzymes which act hydrolytically. The newest enzyme is by no means the least interesting, as it partakes of the nature of an oxydase; it has been dubbed *β -hydroxybutyrase* by its discoverers, Dakin and Wakeman,²⁰ for it is the agent responsible in the body for the conversion of *β -hydroxybutyric acid* into acetoacetic acid. It is present in the liver cells and in aqueous extracts of the liver. Its action is increased by the addition of blood, or of crystallised oxyhæmoglobin, which furnish readily the necessary oxygen. The liver tissue also decomposes acetoacetates with the formation of acetone, but here the addition of blood produces no increase in the action, which is probably what one would expect, seeing that the action is not an oxidative one.

Blood Coagulation.—Here we have to deal with enzymic activity also, and enter a field of controversy which has been comparatively quiescent during the last few years. The work of Morawitz had provided, at any rate, a working hypothesis, which to a great extent explained and harmonised previously conflicting views. One disturber of this placid state has been J. Mellanby,²¹ many of whose experiments do not support Morawitz's view of the causes of blood coagulation. Mellanby's theories, however, run on the same lines as those of Morawitz; the differences are those of detail concerning the relative importance of thrombin and kinase in producing clotting, and of anti-thrombin and anti-kinase in restraining it.

¹⁸ *University of California publications in Physiology*, 1909, 3, 115.

¹⁹ W. Sigmund, *Monatsh.*, 1909, 30, 77; *A.* i, 277.

²⁰ *J. Biol. Chem.*, 1909, 6, 373; *A.* ii, 908.

²¹ *J. Physiol.*, 1909, 38, 28, 441; *A.* ii, 158, 680.

Morawitz,²² moreover, vigorously defends his own theories, and the question is thus in a stage not for final settlement, and one which is mainly interesting to specialists in the subject. B. J. Collingwood's²³ contribution relates to the rôle of calcium in the causation of clotting; he concludes from his experiments that the blood carries calcium in some other way than in a state of simple solution, and that calcium ions are not essential to coagulation. The third disturber of the peace is L. F. Rettger,²⁴ and his views are quite revolutionary, for he doubts whether thrombin is an enzyme at all; he regards the existence of a pro-enzyme as unproved, and the existence of kinase as improbable. He looks on blood coagulation as a quantitative reaction, and probably as a mutual precipitation of two colloids, fibrinogen and thrombin. It will readily be understood that on this view the action of anti-thrombin, calcium salts, and decalcifying agents is interpreted on new lines, but on this and many other points this very suggestive (but far from convincing) paper cannot be advantageously summarised. The whole problem is thus once more in the melting pot.

Mechanical Destruction of Enzymes.—The mechanical precipitation of proteins from solution by shaking has been known for some years, and its discoverer was W. Ramsden (1894). The destruction of enzymes by the same mechanical process is an interesting fact we owe to S. J. Meltzer and his colleagues. The announcement was made late in 1908,²⁵ but the full paper²⁶ has only just appeared, and deals principally with proteolytic enzymes. Other workers, references to whose writings are given fully in the paper, have, however, confirmed the same statement in reference to other enzymes.²⁷

It might be supposed that this is due to the proteins being precipitated and carrying down the enzymes with them, even although the particles are too small to cause perceptible turbidity; a second interpretation would assume that the enzyme remains adherent to the walls of the bottle in some such way as it is adsorbed by fibrin. Such explanations do not, however, commend themselves to Meltzer. Numerous previous experiments have established that shaking is capable of fundamentally influencing bacteria, yeast, blood corpuscles, and starfish eggs, and Meltzer

²² *Biochem. Zeitsch.*, 1909, **18**, 30; *A.*, ii, 592.

²³ *Proc. physiol. Soc.*, 1909, lxxix.; *J. Physiol.*, **38**; *A.*, ii, 681.

²⁴ *Amer. J. Physiol.*, 1909, **24**, 426; *A.*, ii, 680.

²⁵ *Proc. Amer. Physiol. Soc.*, 1908, xxix.; *Amer. J. Physiol.*, **23**; *A.*, i, 277.

²⁶ *Amer. J. Physiol.*, 1909, **25**, 81; *A.*, i, 980.

²⁷ See, for instance, H. C. Bradley, *J. Biol. Chem.*, 1909, **6**, 133; *A.*, ii, 496, in reference to pancreatic lipase; also Harlow and Stiles, *ibid.*, 359; *A.*, i, 861, in reference to ptyalin.

assumes that the nature of the destruction of enzymes is similar to that which takes place in the destruction of living cells, and that shaking affects a certain structure which is common to living cells and to ferments. This, of course, may be perfectly correct, but it brings us no nearer to the real explanation of why shaking is harmful in both cases, and the terms, "molecular disintegration" and "disbanding of the physiological units," which he employs are dangerously like the blessed word Mesopotamia and other shibboleths.

Hormones.

Secretin.—The composition of many of the chemical messengers of the body is still unknown. It is certainly the case for secretin, the first substance to which the general term hormone was applied. The suggestion that it is identical with choline has been abundantly disproved by the work of Dixon and Hamill.²⁸ Their view regarding the way in which it acts on the pancreas advances our understanding of the processes in which it participates. As is well known, there are three enzymes or potential enzymes in the pancreatic juice, namely, trypsin, amylopsin, and steapsin (or, better, lipase); the two last-named are present in the juice ready for action on starch and fat respectively; the proteolytic enzyme, however, is in the condition of a pro-enzyme termed trypsinogen, and the conversion of this into the active enzyme is the work of the enterokinase of the intestinal juice.²⁹ The two ready formed enzymes and the one which requires activation are present in the pancreatic cells as mother substances, which may respectively be termed pro-trypsinogen, pro-amylopsin, and pro-steapsin. Secretin, according to Dixon and Hamill, acts chemically on all three, and liberates trypsinogen in the first case, and the two active enzymes in the last two cases. What the nature is of the chemical interaction between secretin and the zymogens is not known; Dixon and Hamill are inclined to regard it as combination, but Mellanby³⁰ has cited certain facts which he thinks renders this view untenable.

Adrenaline.—This, on the other hand, is an instance of a hormone about which physiologists and chemists can congratulate themselves in having discovered the chemical constitution.³¹ Of its two

²⁸ *J. Physiol.*, 1909, **38**, 314; *A.*, ii, 414.

²⁹ On the activation of trypsinogen by another agency, namely, calcium salts, see B. Ayrton, *Quart. J. exp. Physiol.*, 1909, **2**, 201; *A.*, ii, 497. On the date at which the digestive enzymes appear in the human embryo, see J. Ibrahim (*Biochem. Zeitsch.*, 1909, **22**, 24; *A.*, ii, 1034).

³⁰ *Proc. physiol. Soc.*, 1909, xi.; *J. Physiol.*, **39**; *A.*, ii, 683.

³¹ On recent syntheses in the adrenaline or epinephrine series, see Tutin, Caton and Hann, *Trans.*, 1909, **95**, 2113.

isomerides, the one which occurs in nature (*l*-adrenaline) is far more powerful in its various physiological activities than the *d*-adrenaline. This was first shown by Cushny,³² and Cushny's work has been corroborated by Abderhalden and his colleagues in a series of papers.³³ The racemic base has an intermediate power proportional to the amount of *l*-adrenaline it contains. An interesting point has arisen from Abderhalden's work in relation to so-called "adrenaline immunity"; for in mice, dosage with the inactive or *d*-base renders these animals more resistant to the subsequent action of the active base. This, however, was found not to hold for higher animals, such as dogs.³⁴

Pressor Bases in Putrid Meat.—This question follows naturally after a consideration of adrenaline, as will be seen immediately, and is, moreover, an example of how research on the unpleasant products of putrefaction has been followed by practical results which are not unimportant. We may take as our starting point the work by Abelous³⁵ and his colleagues on the bases present in putrefying horseflesh. They did not succeed in identifying their product chemically, but they showed that on injecting it into the blood stream it produces a rise of arterial blood-pressure somewhat similar to that caused by adrenaline. They further found a base with the same properties in the urine, and surmised (correctly, as it turned out) that this substance is formed by putrefactive processes in the intestine, from which it is absorbed, finally leaving the body in the urine. They named it *urohypertensine*, and they subsequently supported their view of its origin by discovering it in the fæces.

Quite independently of this, Dixon and Tayler found that extracts of the placenta have a similar adrenaline-like action, and they surmised (incorrectly, as it turned out) that it was a normal internal secretion of the placenta, and that its use came into play during and after delivery in causing uterine contraction. This brings us to the beginning of this year, and we have now to deal with the development of the subject during the last twelve months. Rosenheim³⁶ showed that extracts of the placenta have no such action if putrefaction is excluded, and that the pressor substance, or rather substances, are products of initial putrefaction. The

³² *J. Physiol.*, 1908, **37**, 13; *A.*, 1908, ii, 720; *ibid.*, 1909, **38**, 259; *A.*, ii, 420.

³³ *Zeitsch. physiol. Chem.*, 1908, **58**, 185, 189; **59**, 22, 129; **62**, 404; *A.*, ii, 159, 333, 420, 1041.

³⁴ So far as mice are concerned, Abderhalden's statements have been recently confirmed by Waterman (*Zeitsch. physiol. Chem.*, 1909, **63**, 290; *A.*, 1910, ii, 59).

³⁵ *Compt. rend. Soc. Biol.*, 1906, 430.

³⁶ *J. Physiol.*, 1909, **38**, 337; *A.*, ii, 416.

autolytic enzymes without the aid of micro-organisms are unable to split off the terminal carboxyl group of the amino-acids from which they originate. The most active substance separated out was identified as *p*-hydroxyphenylethylamine, and the identity of another with *iso*amylamine was considered probable. In fact, the bases are the same as those found by Barger and Walpole,³⁷ who, on repeating Abelous' work, were successful in discovering the composition of his urohypertensine. The bases are derived quite simply from amino-acids by the loss of carbon dioxide; *iso*amylamine is in this way derived from leucine, and *p*-hydroxyphenylethylamine from tyrosine. The second is by far the more powerful physiologically, as perhaps one would anticipate from its closer relationship to adrenaline.³⁸ A third base, probably phenylethylamine (from phenylalanine), was separated out in smaller amount. They consider it probable that Abelous' base is mainly *iso*amylamine.

W. Bain³⁹ then took up the subject from the clinical point of view, and at present he has only published a preliminary account of his investigations. He separated out the bases from normal urine, and, although they are present in such small quantities that sufficient was not available from this source for analysis, there can be practically no doubt, from their chemical and physiological properties, that their composition is that of the two bases just mentioned. From the practical point of view of the physician, the question arises: Would the retention of such bases in the body account for the high blood-pressure seen in disease? And in the few cases up to now examined, his results show that in gout and allied conditions they are scanty or even absent in the urine, and so it would appear that the question must be answered in the affirmative. But while awaiting further investigation, it is interesting to note that the subject has had another important practical side issue, for Barger and Dale⁴⁰ have shown that the same two bases, and especially the more powerful one, are present in extracts of ergot of rye. This explains the effect of ergot in raising arterial pressure, which previously it was difficult to attribute entirely to ergotoxine. Their effect on the uterus is also marked, and so the introduction of a pure drug has been rendered possible, and the notorious variability of extracts of ergot need no longer be a serious difficulty.

³⁷ *Proc. physiol. Soc.*, 1909, xxiii; *J. Physiol.*, **38**; *A.*, ii, 254; *J. Physiol.*, 1909, **38**, 337; *A.*, ii, 416.

³⁸ On the relative power of these and other amines, see Dixon and Dale, *J. Physiol.*, 1909, **39**, 25; *A.*, ii, 688.

³⁹ *Lancet*, Aug. 7, 1909.

⁴⁰ *Proc. physiol. Soc.*, 1909, lxvii.; *J. Physiol.*, **38**, *A.*, ii, 689.

The Pineal Gland and Pituitary Body.

The suprarenal gland and the thyroid are instances of the ductless glands, the function of which has been elucidated by biochemical research; it has been shown that they produce internal secretions which are essential for healthy life, and the method of experimenting with extracts of the organs has played no mean part in the solution of their functions. It now looks as if we are on the eve of being able to chronicle the discovery of the function of one of those little outgrowths of the brain the names of which stand at the head of this section.

The Pineal Gland.—We will take this first, because it is the one of which we know least from the physiological point of view. It received its name from its resemblance in shape to a pine cone, and obtained celebrity from the fact that Descartes localised here the seat of the soul, mainly because it was the one structure in the brain which was not paired. Recent researches by morphologists have, however, shown that even this slender piece of evidence is incorrect. Originally the outgrowth is paired, and in some parts of the animal kingdom both outgrowths attain considerable complexity; one of the pair becomes developed into a median sense organ, the so-called pineal eye, which is connected to the brain by a nerve, and which is doubtless sensitive to light, although covered by skin; this is seen in certain fishes, such as the lamprey, and in a good many lizards, notably the Tuatara or Hatteria, the New Zealand lizard. The member of the pair of outgrowths which becomes the pineal eye in the lamprey becomes in the lizard a complex glandular structure called the pineal gland, and the other one becomes the pineal eye. In mammals, man included, the pineal eye has entirely disappeared, and the pineal gland is atrophied and calcareous. It probably is a functionless, vestigial structure, and extracts of it produce, on injection into animals, no physiological effects.⁴¹

The Pituitary Body.—This is an outgrowth from the base of the brain, which in man weighs about half a gram, and until recently it also was regarded as an ancestral vestige, or at least of but little importance, in spite of the fact that it possesses an elaborate structure. It is situated in the bony depression at the base of the skull known as the Turkish saddle (*Sella turcica*), and owes its name to the view of the ancients that its function is to secrete the pituita or mucus of the nose.

We now know that it is a structure which, like the thyroid and suprarenal, is indispensable to life, and that it exerts its influence

⁴¹ Dixon and Halliburton, *Quart. J. exp. Physiol.*, 1909, 2, 283.

on the metabolism of the body by the formation of an internal secretion which contains hormones. The chief point on which we are still in ignorance is the composition of these chemical messengers.

From the developmental point of view it consists of two parts: one of these is nervous in origin, and is a downgrowth from the brain in the region of the third ventricle, with which it remains connected by a funnel-shaped stalk known as the infundibulum; at first this growth is hollow, and traces of the original cavity are seen in some animals, but in the majority of animals the cavity is obliterated by the growth of neuroglia. This nervous portion of the pituitary constitutes its posterior lobe, but in the adult it shows little or no true nervous structure, being made mainly of interstitial or neuroglial tissue. The other part of the pituitary is an upgrowth from the mouth, which meets the nervous downgrowth, and the two parts fuse together. The original connexion with the buccal cavity is soon cut off by the completion of the roof of the mouth. This island of epithelium cells from the mouth is hollow; but as the cells multiply, the walls of the sac become thickened, and ultimately only a cleft remains; the cells on one side of this cleft apply themselves to the posterior lobe, which they cover and invade; this constitutes the *pars intermedia*; it is here that colloid material is formed, which collects in cysts, reminding one of the colloid acini of the thyroid gland; and it is probably owing to these cells that the posterior lobe possesses the physiological properties to be immediately described; the colloid material passes along the remains of the cleft into the third ventricle of the brain. The rest of the buccal outgrowth is developed into the anterior lobe proper, the largest portion of the organ; this is very vascular, and the cells, many of which are granular, possess a well-marked glandular appearance.⁴²

The first investigator who recognised the importance of the pituitary was P. Marie (1885), who pointed out that the disease to which he gave the name of *acromegaly* is associated with an overgrowth of the pituitary body. This disease is a chronic one, which affects adults, and is characterised by a peculiar overgrowth of the lower jaw and of the extremities. A giant, thanks to our nursery legends, is usually regarded as an extremely powerful person; as a matter of fact gigantism is usually a pathological condition associated with sterility and other weaknesses, and closely allied to acromegaly. The late Prof. Cunningham, of Edinburgh,

⁴² These facts, as well as others relating to function, especially of the posterior lobe, we owe to a series of papers by Schäfer, Herring, and their colleagues, published in the first 2 volumes of the *Quarterly Journal of Experimental Physiology*.

found in the skeletons of the giants he examined a great enlargement of the sella turcica, which proved that they had large pituitaries. The question has arisen whether the condition is due to destruction of the pituitary structure and consequent loss of an internal secretion, which was the view originally advanced by Marie; or, on the other hand, the view has been advanced that the symptoms of gigantism and acromegaly are due to a hypertrophic condition, in which too great a quantity of a hormone is produced, which stimulates the growth of the skeletal structures. This second view is the one generally adopted to-day, first because complete destruction of the organ leads to almost immediate death, secondly because feeding on pituitary does not diminish but increases the pathological condition, and thirdly because hypertrophy of the anterior lobe is associated normally with the growth of the skeleton in young individuals. Feeding young animals on the anterior lobe increases their rate of growth.⁴³ The conclusion to be drawn from this and other observations of a similar nature is that the function of the anterior lobe is related to the growth of the skeletal tissues, including cartilage, bone, and connective tissue in general; these effects are probably produced by hormones secreted by the glandular cells before referred to. In the obtaining of this knowledge, it will be noted that the method of injecting extracts has played no part; in fact, the intravascular injection of an extract of the anterior lobe produces hardly any physiological effect at all; one only notices a slight and transient fall of arterial blood-pressure, which is the usual effect produced by most tissue extracts.

Quite otherwise is the history of our knowledge in reference to the posterior lobe; this has been almost entirely elucidated from the effects observed when extracts of this portion of the organ are injected into the blood stream. These effects are almost certainly due, not to the posterior lobe proper, but to the cells of the pars intermedia which invade it and its stalk, and to the colloid material which those cells produce.

The first investigations of this kind were performed by Schäfer and Oliver (1895) shortly after they had published their epoch-marking work on the suprarenal. They found that aqueous or saline extracts of the pituitary were the only extracts of tissues except the suprarenal which produce a rise of arterial pressure. They found that the efficacy of such extracts was not impaired by boiling, and that, although the rise of blood-pressure is produced by constriction of peripheral vessels, there were certain points of detail which distinguished the action from that of adrenaline.

⁴³ See Schäfer, Croonian lecture, *Proc. Roy. Soc.*, 1909, B, **81**, 442.

Three years later Howell, of Baltimore, took the matter up, and ascertained that the rise of pressure was entirely due to the posterior lobe. He also showed that the substance responsible for the action could not be adrenaline, for if a second dose is injected within a certain time the effect is not repeated; in other words, a certain amount of immunity is established which only slowly passes off.

The non-existence of adrenaline in the pituitary has, since that time, been determined by chemical tests, and within the last few weeks H. H. Dale⁴⁴ has shown another physiological difference between the two substances; adrenaline exerts its action by stimulating sympathetic nerve-endings, whereas pituitary extracts stimulate involuntary muscle directly. Repeated injections produce no true immunity in the sense that immune substances are developed in the blood.⁴⁵

Schäfer and Vincent repeated Howell's observations, and confirmed them, and since then the action of pituitary extract in stimulating other forms of involuntary muscular tissue has been noted, and among these the pupil and the uterus may be specially mentioned. This fact, as well as the fact that the pituitary rise of blood-pressure is of considerable duration, has led to the introduction of the extract as a therapeutic agent⁴⁶; it is a little early to say whether the somewhat extravagant praise bestowed upon it in producing uterine contraction after delivery is really warranted.

The most remarkable action which the extract has is not, however, on muscular tissue at all, but on the kidney. In this organ there is vaso-dilatation instead of constriction, and an abundant flow of urine is produced; the discovery of this is due to later work by Schäfer in conjunction with Magnus and Herring. The cases of acromegaly, in which polyuria has been described as a symptom, are really produced by an invasion of the posterior lobe.

These facts, which are the result of experiments on animals, have now been confirmed in the case of the human pituitary,⁴⁷ the posterior lobe of which alone exhibits the characteristic effects on blood-pressure and kidney. Whether other epithelial structures besides the kidney are stimulated has still to be discovered. It certainly seems a roundabout way to reach the kidney by way of the third ventricle of the brain; still, the relationship of the renal and pituitary organs is undoubted and most marked. Schäfer

⁴⁴ *Bio-Chem. J.*, 1909, **4**, 427; *A.*, ii, 1036.

⁴⁵ It would be interesting to ascertain whether Abderhalden's adrenaline immunity, alluded to on p. 177 of this report, is a true immunity in this sense also.

⁴⁶ See, for instance, Blair Bell, *Brit. Med. J.*, Dec., 1909.

⁴⁷ Halliburton, Candler, and Sikes, *Proc. physiol. Soc.*, 1909, xxxvii.; *J. Physiol.*, **38**; *A.*, ii, 417; *Quart. J. exp. Physiol.* 1909, **2**, 280.

and his colleagues attribute the actions of the extract to separate hormones, one acting on the muscular, another on the kidney tissues, but Dale is inclined to the view that it is not necessary to suppose that more than one chemical stimulus is at work. It should be added that in Schäfer's last contribution to the subject (Croonian lecture) he has shown that both in animals and children the addition of a small and regular amount of the posterior lobe of pituitary to their food produces an increase in the urine secreted.

Finally, an important fact in the physiology of the pituitary body is that this organ, small though it is, is indispensable to life, and therefore should not be removed surgically in man. Paulesco found, and his results have been confirmed by Harvey Cushing, of Baltimore, that removal of the organ in animals is invariably fatal, usually within forty-eight hours. Cushing⁴⁸ also has succeeded in averting the fatal issue in dogs by transplanting it immediately after removal into the cortex of the brain. He also observed that marked polyuria follows the transplantation of the entire gland, that it disappears after extirpation of the transplant, and that it does not follow transplantation of the posterior lobe alone; this last fact seems to indicate some mutual relationship of the two lobes in the production of the hormone responsible for the diuretic effect.

It is not yet known which part of the pituitary is essential to life. It is almost impossible to remove one part alone, so closely are they dovetailed into one another. It is quite possible here also there may be a corresponding dovetailing of function.

Paulesco states that the mere separation of the pars nervosa from the infundibulum is as fatal as the actual removal of the organ. In view of the discovery by Herring that the secretion of the pars intermedia discharges into the infundibulum and third ventricle, this statement of Paulesco is of great interest, but it still awaits confirmation.

Our knowledge of the chemistry of the hormones of the pituitary is negative rather than positive. We know absolutely nothing of the secretion of the anterior lobe, which controls skeletal growth. But, seeing that the extract of the posterior lobe is physiologically active, it is probably only a matter of time before biochemists make themselves acquainted with the hormone (or hormones) it contains.

We at least know that the physiologically active substances are not protein, for the extracts can be boiled without impairing their activity. We further know that the pressor substance is not adrenaline for the reasons already given; and, finally, we are now quite certain that the colloid material present is not the same

⁴⁸ Cushing, Crowe, and Homans, *Quart. J. exper. Physiol.*, 1909, 2, 389.

material as the colloid of the thyroid gland, since it contains no iodine.

The similarity in histological appearance of the two colloids gave support to the idea that the pituitary can act vicariously for the thyroid in cases of thyroid insufficiency. Removal of the thyroid certainly leads to an increase in the size of the pituitary and of the colloid material it secretes, but extirpation of the thyroid also modifies the growth of many other tissues and organs in the body, and there is really no ground for the hypothesis that the two organs have any common ground of action. Disease or removal of the pituitary produces quite different effects from those observed when the thyroid is diseased or removed. Injection of extracts gives widely divergent results; and the last shred of support to the view is now given by the demonstration of the absence of iodine in the pituitary body.

Baumann, soon after his discovery of thyriodin, looked for iodine in the pituitary with negative results. One or two observers, it is true, have stated that they have obtained traces, but their work will not bear close investigation. I⁴⁹ found that it is entirely absent both in the normal human and bovine pituitary; and Simpson and Hunter⁵⁰ have obtained the same negative result in sheep's pituitaries after the thyroid gland had been extirpated.

On the positive side, I can find only two researches, and these have both been published at present in preliminary form only. One of these is by T. B. Aldrich,⁵¹ who succeeded in separating a base from the organ, from which a crystalline picrate and sulphate were prepared. These salts had a pressor effect. The other is by Allers⁵²; he found no adrenaline and no *o*-dihydroxybenzene derivatives, but he attributes the pressor action to a substance which, like adrenaline, contains alkylated amino-nitrogen.

Thus for the present we must leave this interesting subject, and although there is plenty of other material in the work of the year which might be mentioned and is of undoubted importance, nevertheless, exigencies of space compel me to close the report at this point.

W. D. HALLIBURTON.

⁴⁹ Halliburton, Candler, and Sikes, *loc. cit.*

⁵⁰ *Proc. Soc. Experim. Med. and Biology*, New York, 1909, **7**, 11.

⁵¹ *Proc. Amer. Physiol. Soc.*, 1907-8, xxiii; *Amer. J. Physiol.*, **21**.

⁵² *Münch. med. Woch.*, **56**, No. 29, July, 1909.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE year 1909 has not shown any marked increase or diminution in the number of publications, but, so far as regards England at least, there seems to be some promise of its eventually being regarded as a "vintage year," on account of the publication of Russell and Hutchinson's paper on the function of the protozoa in the soil, which does represent an entirely novel idea. Otherwise there is nothing of special interest to chronicle, although in many directions the investigations that are reported assist considerably towards the construction of a firm and coherent theory of plant and animal nutrition.

At the International Congress of Applied Chemistry, held in London during the year, there was a long list of papers on Agricultural Chemistry, but it cannot be said that they resulted in very fruitful discussions. The majority of the papers consisted of detailed communications of interest only to specialists, and when the subject was of a more general character the language difficulty was a great check on free discussion.

Soil Bacteriology.

In my Annual Report for 1907 ¹ I gave an account of some work by F. V. Darbyshire and E. J. Russell on the action of heat and of volatile antiseptics on soil, in which they had shown, in agreement with the observations of a number of other investigators, that the fertility of the soil can be very greatly increased by such treatment. For example, all the soils they examined, if heated to a temperature of 100° for two hours, would yield twice as great a crop as the same soil untreated, when the two were afterwards cultivated under similar conditions in pots. Exposure to the vapour of carbon disulphide, chloroform, or toluene for forty-eight hours, followed by complete evaporation of the antiseptic, resulted in an increased yield of about 30 per cent. Various theories have been advanced to account for the increased availability of the plant food in the soil which results from treatment of this kind.

¹ *Ann. Report*, 1907, 264.

S. U. Pickering, for example,² has shown that the heating, and even the treatment with antiseptics, are followed by a marked increase in the amount of soluble nitrogen compounds that can be extracted from the soil, which extra available plant food he regards as sufficient to account for the increase of crop. More generally it was supposed that some change in the bacterial flora of the soil had been effected, which resulted in a greater availability of the original stock of nitrogen, or perhaps brought about increased fixation of free atmospheric nitrogen, but the mechanism was not clearly understood. Russell and Hutchinson,³ working in the Rothamsted laboratory, have arrived at another solution. They began by finding, in common with other observers, that the treatment to which the soil was subjected by no means effected complete sterilisation. The numbers of bacteria were enormously reduced by the process if they were counted immediately afterwards, but when the soil was moistened and put under conditions suitable for growth, the numbers rapidly mounted up again, and eventually reached a magnitude which was never attained under normal conditions in the untreated soil. For example, a Rothamsted soil contained at the outset about 7,000,000 organisms per gram, a number which remained comparatively constant on storage; after heating, the number had fallen to 400 per gram; and after treating with toluene, to 2,600,000. Four days later, however, these small numbers had risen in the case of the heated soil to over 6,000,000, after which it ceased to be possible to count the colonies; in the case of the toluene the numbers rose to 40,000,000 in nine days. *Pari passu* with this increase in the number of the bacteria in the soil came an increase in the rate at which ammonia was produced by the breakdown of the more complex carbon compounds of nitrogen that were present in the soil. When no plants were present to take up this ammonia, it accumulated in the soils, because the bacteria which convert nitrites and nitrates had been completely destroyed. It thus appeared pretty clear that the increased fertility of the treated soils was due to their greater power of breaking down the complex organic matter of the soil to the state of ammonia, a form in which plants can assimilate nitrogen; and this increased production of ammonia was due to an exceptional multiplication of the ammonia-splitting organisms which constitute so large a proportion of the normal bacterial flora of the soil. The authors then carried out various experiments, which showed (1) that no stimulus could be supposed to have taken place through the treatment which would make the bacteria remaining in the soil more active; (2) that there had been no selective destruction of organisms

² *J. Agric. Sci.*, 1908, 2, 411; 3, 32,

³ *Ibid.*, 1909, 3, 111,

which would leave behind a population of a more active type than the usual mixed flora of the soil. By other steps which need not be here set out, it became clear that the difference between the treated and untreated soils was due to some factor in the latter which normally limits the number of bacteria, and therefore the rate of production of ammonia. Search for this unknown factor disclosed the presence, in all soils so far examined, of numbers of protozoa and amoeba, which live on bacteria and keep their numbers down to the comparatively low limit specified. The heating or treatment with antiseptics kills off all these large organisms, but leaves unhurt some spores of the ammonia-producing bacteria, which afterwards can develop to a much greater extent than in the untreated soil because they are freed from their normal check.

The theory as it stands then assumes that, putting aside its physical characteristics, the fertility of a soil is determined by the activity, or rather by the number, of its ammonia-producing bacteria, and the number is kept in equilibrium by the activity of the protozoa for which these bacteria serve as food. Any cause which destroys or reduces the number of the protozoa enables the bacteria to extend their territory, and so raises the fertility of the soil. The authors have also carried out a number of collateral experiments, which show that the direct additions of these large organisms will rapidly reduce the activity of various fermenting media, but this and other positive evidence in favour of the theory have not as yet been published in full. Many of Russell and Hutchinson's observations on the increase in the number of bacteria and in ammonia production which is brought about by antiseptics are confirmed in a paper by K. Störmer,⁴ although this author has not arrived at any valid explanation of his experimental results.

It will be seen that this addition to the theory of the vital actions going on in the soil, not only serves to explain a large number of observations which have been accumulating for some years past (for example, Rahn's⁵ work on the effect of drying soil), but it is likely to lead to widespread applications in practice. It has always been difficult to understand why the number of bacteria in the soil was not greater, and why it varied so little with the seasons; but now we see that a limiting factor exists affected in the same way by changes of temperature and humidity. Whatever may be the practical outcome of Russell and Hutchinson's work, this new point of view they have given us represents the most notable addition to the theory of the soil since the publication of Hellriegel and Wilfarth's paper on the nodule bacteria in 1886.

⁴ *Jahresber. Vereinigung angew. Bot.*, 1908, 113; *A.*, ii, 608.

⁵ *Ann. Report*, 1907, 265.

Turning to some of the older questions of soil bacteriology, nitrogen fixation by means of *Azotobacter* continues to occupy the attention of a large number of investigators, although no specially novel fact has emerged during the course of the year. T. Remy⁶ has examined the carbohydrates which will serve as sources of energy for the fixation of nitrogen in soils, and finds that humus is able to supply the necessary carbohydrate, so that there is always some fixation taking place in any soil containing humus and calcium carbonate. In acid soils and in peat no fixation is going forward. Magnesium and calcium carbonate are equally effective bases, both of them being better than the soluble sodium and potassium carbonates. Remy also repeated Koch's experiments,⁷ in which soil in pots was mixed with sugar to the extent of as much as 2 per cent. If these soils were then incubated for a few weeks and plants grown in them, much better crops were produced than in the control pots where no sugar had been used. In Remy's experiments the soil with sugar gained 141 milligrams of nitrogen per kilo., and this was left in compounds which soon became available for the plant, as shown by the growth of the ensuing crop.

H. Pringsheim⁸ has also been investigating the availability of cellulose as a source of energy in nitrogen fixation, examining, however, anaerobic fermentations of *Clostridium* and similar organisms. He obtained a fixation of considerably higher quantities of nitrogen by these organisms per gram of carbohydrate consumed than had been observed by the previous workers with the anaerobic bacteria.

One of the most interesting papers dealing with soil bacteria has been contributed by M. W. Beyerinck and D. C. J. Minkman⁹ on the relationship of bacteria to the formation and utilisation of nitrous oxide. By inoculating cultures containing potassium nitrate and organic matter with various soils and incubating them in absence of oxygen, they have picked up and identified a number of organisms which will reduce the nitrate to nitrous oxide, nitrogen gas, and ammonia, the relative proportion of these three products depending to a large extent on the concentration of the solution. Besides identifying the denitrifying organisms originally observed by Gayon and Dupetit, they isolated two other organisms, which are probably the destroyers of nitrates in soil. One of these organisms is so active that from a good large culture a stream of gas is evolved containing about 80 per cent. of nitrous oxide and capable of rekindling a glowing splint presented to the orifice of

⁶ *Centr. Bakt. Par.*, 1909, ii, 22, 561; *A.*, ii, 340.

⁷ *Ann. Report*, 1907, 261.

⁸ *Centr. Bakt. Par.*, 1909, ii, 23, 300. ⁹ *Ibid.*, 25, 30; *A.*, ii, 1043.

the exit tube. The fermentation seems so much under control that this might make an effective lecture table experiment. The authors then proceed to consider the fate of the nitrous oxide, which must always be thus arising in the soil, and show that several organisms can take away its oxygen to set free nitrogen. Finally, they show that in the soil there exists an organism capable of bringing into combination a mixture of hydrogen and nitrous oxide, from which combination it derives the energy necessary to decompose carbon dioxide and utilise the carbon for its own structure. The experiment is a very simple one; a culture solution, containing no organic matter but the usual nutrient salts and a little sodium bicarbonate, is inoculated with a trace of soil, and is then left in contact with the mixture of equal volumes of hydrogen and nitrous oxide. The gases slowly disappear, and at the same time the culture solution becomes covered with a thick scum formed by an organism, the organic matter of which has been synthesised from the carbon of the carbon dioxide and the nitrogen of the nitrous oxide, while the necessary energy has been derived from the union of the two gases.

H. Fischer¹⁰ has examined the effect of liming the soil on the bacteria contained therein, chiefly from the point of view of the behaviour of ammonium salts on soils rich in calcium carbonate. He finds, with other observers, that when either sodium nitrate or ammonium sulphate is supplied to the soil, some of the nitrogen is utilised by soil bacteria and converted into proteins. This action Fischer finds to be increased by calcium carbonate in the case of ammonium salts, but not in the case of sodium nitrate, as indeed would be expected from the physiological acidity of the former compound. To this he attributes the lower manurial effect of ammoniacal nitrogen as compared with nitrate nitrogen, rather than to any evaporation of ammonia set free by the calcium carbonate from the soil.

A paper of considerable technical interest by S. Bierema¹¹ compares the various nitrogen compounds, such as nitrates, ammonium salts, amides, and amino-acids, as sources of nitrogen for the cultivation of soil organisms, the experiments being made both with pure cultures and a mixed inoculation with ordinary soil. These sources of nitrogen are also combined with different carbohydrates and other sources of carbon, and although no general conclusions can be drawn from the results, the worker who desires to make up the most suitable medium for the cultivation of particular organisms may there find much information of value.

¹⁰ *Landw. Versuchs-Stat.*, 1909, **70**, 335; *A.*, ii, 602.

¹¹ *Cent. Bakt. Par.*, 1909, ii, **23**, 672; *A.*, ii, 692.

R. W. Stigell¹² reports a series of experiments on the influence of heavy inoculations of various common putrefactive bacteria, such as *B. megatherium*, *B. subtilis*, *B. pyocyaneus*, on the germination of seeds and the development of young roots. The author found that the bacteria had but a small and irregular effect on the plants at any stage in their development, in spite of the numbers of the bacteria in the medium.

Soil Physics.

A. Müntz and H. Gaudechon¹³ have given us very elegant demonstration of some points in the behaviour of soluble salts, like sodium nitrate, when applied as fertilisers to the soil. Taking boxes of fairly dry soil, they introduced here and there on the surface a crystal of sodium nitrate, and observed that after a time a moist spot grew round the crystal, marked by a change of colour in the soil. This moist spot was formed by water which had been drawn by the salt from the surrounding soil. The salt itself dissolved, but did not diffuse laterally outside the area of the moist spot. Similarly, in wet soil, the crystals formed a zone of dissolved salt round them, but diffusion either laterally or vertically was extremely slow, and did not extend more than 2.5 cm. in six days. When the boxes were further exposed to fine rain, the salts were carried vertically downwards with very little lateral diffusion, forming very steep-sided cones of soil within which the salt could be traced. The authors conclude that very little movement of soluble manurial salts takes place in the soil by diffusion. The Rothamsted experiments afford a number of interesting illustrations on this point. For example, on the grass field, the effect of an application of 550 lb. per acre per annum of sodium nitrate for the last fifty-three years does not extend a foot over the boundary line of the plot, the change in the character of the herbage being quite sharp and decided at the edge of the plot.

The question of the nature of clay, and the flocculation of suspensions of such fine particles, continues to attract a good deal of investigations, but I cannot see that the subject is being materially advanced. The experimental facts remain much as they were summarised in 1907,¹⁴ and the explanations offered are only verbal. W. Funk¹⁵ powdered felspar very finely and obtained a colloidal suspension when it was mixed with water; at the same time chemical change had taken place, as was shown by the fact that the water became alkaline. When the water contained carbon

¹² *Cent. Bakt. Par.*, 1909, ii, 23, 727.

¹³ *Compt. rend.*, 1909, 148, 253; *A.*, ii, 259.

¹⁴ *Ann. Report*, 1907, 269.

¹⁵ *Zeitsch. angew. Chem.*, 1909, 22, 145; *A.*, ii, 146.

dioxide, the attack on the felspar was greater, but there was less tendency to form a colloid suspension. P. Rohland¹⁶ has also examined the nature of the substances forming suspensions in water. He tried powdered talc, alumina, ultramarine, calcium carbonate, calcium sulphate, felspar, etc., with water, but found that only those materials formed true suspensions which react with water to produce colloidal substances. It will be noticed that these results simply confirm the conclusions reached by Morison and Hall¹⁷ in 1907.

E. Blanck¹⁸ has investigated the effect of a mixture of calcium carbonate or lime on the physical properties of the soil. He finds that calcium carbonate increases the percolation through the soil, but not its power of capillary lifting, whilst it diminishes its water-holding capacity. Lime, on the contrary, increases the water-holding capacity, but diminishes the capillary uplift and the percolation. These observations also are explicable by the difference in the flocculating power of calcium bicarbonate and calcium hydrate observed by Morison and Hall (*loc. cit.*).

In continuation of their work on the organic substances contained in soil, which were discussed in my last report, Schreiner and Shorey¹⁹ have isolated another crystalline substance from the organic matter of soil. By extraction with alcohol and ether of a clay soil containing more than 16 per cent. of organic matter and 0.5 per cent. of nitrogen, they obtained a cholesterol-like substance of the empirical composition $C_{26}H_{44}O$, to which they have given the name of agosterol, because it gives Liebermann's cholesterol reaction. Its significance in the behaviour of the soil is not yet apparent.

The question of the function of roots in rendering the mineral matter of the soil available for plant food has always been a matter of discussion; latterly the increased solution has been generally credited to the carbon dioxide excreted by the roots. E. A. Mitscherlich²⁰ has now shown that an artificial increase in the amount of carbon dioxide in the soil is followed by no increase in production. The roots and the decay of organic matter normally produce sufficient carbon dioxide to give the soil water its maximum solvent action, so that it does not become more effective when an excess of carbon dioxide is added artificially.

E. Haselhoff²¹ also investigated the weathering power of roots by

¹⁶ *Zeitsch. angew. Chem.*, 1909, **22**, 931; *A.*, ii, 474.

¹⁷ *Ann. Report*, 1907, 269.

¹⁸ *Landw. Jahrb.*, 1909, **38**, 715, 863.

¹⁹ *J. Amer. Chem. Soc.*, 1909, **31**, 116; *A.*, i, 152.

²⁰ *Landw. Jahrb.*, 1910, **39**, 157.

²¹ *Landw. Versuchs-Stat.*, 1909, **70**, 53; *A.*, ii, 259.

allowing plants to grow in vessels filled with coarsely powdered rocks of various kinds. He examined their contents after several years, and found that leguminous plants were more effective than cereals, both in growing under such conditions and in reducing the rock to a state of very fine particles.

Chemistry of the Growing Plant.

In the papers of this year less attention seems to have been paid to assimilation than to respiration, on which a good deal of interesting work has been reported. P. B. Jensen²² has been investigating the intramolecular respiration of seedlings under anaerobic conditions, and this he regards as identical with the process of alcoholic fermentation. He fixes on dihydroxyacetone as the intermediate product that is first formed from dextrose, and finds that it yields carbon dioxide and water under the action of oxydase in normal respiration, but carbon dioxide and alcohol under the action of one of the zymase enzymes in absence of oxygen. In many respects, Jensen's conclusions are confirmed by S. Kostytscheff,²³ who does not regard alcohol as a normal product in respiration, because it cannot be transformed by any of the enzymes present into carbon dioxide. He considers that alcohol is produced by a special action in the absence of oxygen from some intermediate product, which would agree with the dihydroxyacetone postulated by Jensen. J. White²⁴ has examined cereal seeds of various ages to ascertain if any connexion exists between the retention of vitality and the presence in the seeds of still active enzymes. Seeds of wheat, barley, oats, maize, and rye would rarely germinate when more than ten years old, but even after twenty years the author found in them diastatic, fibrin-digesting, and ereptic ferments retaining their activity. No relation could be traced between the vitality of the seeds and the persistence of the enzymes, nor did the addition of enzymes enable any of the otherwise non-germinable seeds to germinate.

The author then studied the respiration processes in seeds, and found that many of them gave off carbon dioxide in considerable quantity immediately after harvesting, but that the gaseous exchange ceased as soon as the seeds had become moderately desiccated. The author considers that dry seeds, when stored, are not respiring, and in this respect agrees with other observers. It is, however, difficult to believe that the action is entirely suspended,

²² *Ber. Deut. bot. Ges.*, 1908, **26a**, 666; *A.*, i, 172.

²³ *Biochem. Zeitsch.*, 1908, **15**, 164; *A.*, ii, 173; *Ber. Deut. bot. Ges.*, 1908, **26a**, 665; *A.*, ii, 84.

²⁴ *Proc. Roy. Soc.*, 1909, **B**, **81**, 417.

although one can see reasons for supposing that it must be so slow as to be almost beyond the possibility of measurement.

B. Schulze and J. Schütz²⁵ have been examining the diurnal and seasonal variations in the composition of the leaves of various plants and trees. They find that the diurnal migration, not only of the carbohydrates, but also of nitrogenous compounds and ash is well marked, there being an accumulation during the daylight, followed by a depletion in the night. The seasonal variation gives rise to a maximum richness of the leaf about June, after which the proportions of nitrogen and valuable ash constituents fall off steadily, there being a very considerable withdrawal of nutrient material before the leaf is allowed to fall.

Otto and Kooper²⁶ have also published a paper in which they arrive at the same conclusions, although their investigation dealt with only the nitrogenous compounds in the leaf.

The question of whether higher plants are capable of utilising any compounds of nitrogen other than the nitrates has again been investigated by H. B. Hutchinson and N. H. J. Miller.²⁷ They succeeded in growing wheat and peas in water cultures under sterile conditions, so that neither nitrification nor other bacterial changes could take place in the nutrient supplied. The plants grew normally when supplied with nitrogen only in the form of ammonium salts, and such plants always contained higher percentages of nitrogen than those grown with sodium nitrate under similar conditions. In view of the absence of nitrification in acid soils and the rapid growth of the plants in soil that has been partly sterilised, in which nitrification has also been shown to be suspended (see page 185), it is important to notice that certain differences show themselves in the habit of plants feeding directly on ammonia, for example, an increased percentage of nitrogen in the dry matter, a darker colour of the leaf, and a dwarfer habit. These differences may even be seen on the Rothamsted plots in the open, as though the nitrification of the ammonium salts were not complete even there.

Stoklasa and Ernest²⁸ have returned to the question of the acid secretions from roots. They found that in water cultures in which aeration was defective, the roots of oats, maize, and buckwheat did secrete small amounts of formic and acetic acids. The roots of barley, however, gave rise to very little of these products; with better aeration the acids were completely oxidised to carbon dioxide,

²⁵ *Landw. Versuchs-Stat.*, 1909, **71**, 299.

²⁶ *Landw. Jahrb.*, 1910, **39**, 168.

²⁷ *J. Agric. Sci.*, 1909, **3**, 179; *A.*, ii, 923.

²⁸ *Jahrb. wiss. Bot.*, 1908, **46**, 55; *A.*, ii, 256.

and in no case were mineral acids observed. The carbon dioxide produced in twenty-four hours from the roots varied from 60 to 130 milligrams per gram of dry matter, and when the plants were set to grow in powdered gneiss or basalt, nitrogen only being supplied, the extent of growth was found to correspond with the power of the plant to excrete carbon dioxide from its roots, showing that a plant's attack on the insoluble minerals of the soil is entirely due to the carbon dioxide excreted from the root.

The chemistry of the wheat grain has excited continued attention. T. B. Wood and W. B. Hardy²⁹ have dealt further with the changes in the physical character of gluten when in equilibrium with dilute solutions of acids and alkalis. In his former paper,³⁰ Wood had shown that the gluten of wheat flour loses all consistency when suspended in weak acid of a strength below a certain critical concentration. For different acids, this critical concentration showed no relation to the conductivity of the solution. The cohesion of the gluten was restored by the addition of salts (electrolytes) in small quantities. The authors have now measured the rate of transport of the particles of the hydrosol of gluten in a uniform electric field, which gives a means of measuring the potential difference between the water face and the protein face of each particle of the hydrosol. The curve obtained for such potential differences with various concentrations of acid agrees in form with those expressing the effects of salts on the cohesion of the gluten, whence the authors conclude that the hydrosol of gluten consists of particles surrounded by an electric double layer, on the potential difference between which and the solute the physical state of the colloid depends.

H. J. von Liebig³¹ has examined the sugars in wheat flour, in which he finds 1 to 1.5 per cent. of sucrose and 0.1 to 0.4 per cent. of dextrose. In the dough the reducing sugars increase up to 4 or 5 per cent. through the formation of maltose, but the sucrose suffers a small loss. In the dough fermentation, the maltose rapidly diminishes. The author has also measured the diastatic power of various flours, but finds them only from 1/3 to 1/7 of Lintner's scale, the largest numbers being obtained with coarse, dark flour.

W. E. Brenchley and A. D. Hall³² have studied the progressive changes in the composition of the grain of wheat during its formation and ripening. These authors distinguished three stages—the formation of the pericarp, the filling of the endosperm, and the ripening process. The material forming the pericarp contains a larger proportion of nitrogen in the dry matter, and a smaller

²⁹ *Proc. Roy. Soc.*, 1909, B, **81**, 38; *A.*, i, 341.

³¹ *Landw. Jahrb.*, 1909, **38**, 251.

³⁰ *Ann. Report*, 1907, 273.

³² *J. Agric. Sci.*, 1909, **3**, 195.

proportion of phosphoric acid in the ash, than does the endosperm material. As soon as the endosperm begins to fill, the plant moves into it material which is practically uniform in composition, at all stages, early and late, in the filling. There appears to be no justification for the opinion usually held that the proteins are moved in first and the carbohydrates later. The ripening process is in the main one of desiccation, although there is some change from non-protein to protein. The authors incidentally show that both the nutrition and assimilation of the plant continue to a much later date than has been usually supposed. The total amount of dry matter, nitrogen, and ash in the plant increases to within a fortnight of harvest. In a separate paper, W. E. Brenchley³³ discusses the accompanying changes in the structure of the grain from the date of fertilisation onwards.

In a communication to the International Congress, which has since been reprinted, J. A. Le Clerc and J. F. Breazeale³⁴ describe some experiments to show that annual plants, like wheat, oats, and other cereals, lose considerable quantities of their inorganic constituents through washing by rain. Many previous observers have noticed that the total amount of nitrogen and ash constituents in a plant shows some diminution before the plant finally ripens, and this has been variously attributed to mechanical losses through the fall of dead leaves, etc., or to a physiological excretion by the roots into the soil again. Le Clerc and Breazeale reject the supposition that there is any physiological excretion from the roots, because all the migrations traceable during the growth and maturation of the plant take place from below upwards towards the flowering head. They do find, however, that it is possible to extract by water considerable proportions, particularly of potash and phosphoric acid, from the plant, the losses being greater the older the tissue that is washed, and greatest of all when the tissue is dead. The authors consider that their experiments have considerable bearing on the total amount of plant food removed from the soil by crops growing in the open, and on such matters as the richness in mineral constituents of hay, etc., which has been subjected to rain either before or after cutting. It is certainly often noticeable that when corn crops have stood long in shock and have been much rained on after cutting, there is a noticeable increased vigour of growth in the next crop on the spots on which the stocks had been standing.

A. J. Brown³⁵ has published a further paper on the permeable

³³ *Ann. of Botany*, 1909, **23**, 117.

³⁴ *Year Book of the Dept. of Agric. (U.S.A.)*, 1908, p. 389.

³⁵ *Pro. Roy. Soc.*, 1909, B, **81**, 82; A., ii, 386.

membrane existing in the testa of barley seeds, which permits water to pass into the endosperm, but stops certain other substances. For instance, barley seeds will absorb water from hydrochloric and sulphuric acids, but not the acids themselves, whereas acetic, propionic, formic, and trichloroacetic acids will pass through the membrane. The membrane is impervious to most dissolved salts, but mercuric chloride and cyanide will pass; sucrose, dextrose, and glycerol are arrested by the membrane, but ethyl alcohol, ethyl acetate, and acetone pass through, as also does iodine dissolved in potassium iodide. In none of these cases is there any destruction of the membrane prior to the passage of the selected material.

In an interesting paper on the effect of anæsthetics and of cold on plants, L. Guignard³⁶ finds that these agents bring about interaction between such glucosides and ferments as are present in the leaf. For example, the leaves of crucifers, when strongly chilled or exposed to the vapour of chloroform, give rise to mustard oil. Leaves of *Gaultheria procumbens* give rise to methyl salicylate, whilst cyanogenetic plants form hydrocyanic acid. Probably these observations could be extended to throw some light on the well-known processes of hastening the flowering of plants by etherisation and chilling; they may be compared with the observations of Muller-Thurgau that potatoes become sweet during frost because the enzyme processes producing sugar continue their action, whereas respiration, which destroys sugar, is suspended.

E. Schulze and C. Godet³⁷ have contributed a paper on the carbohydrates of plants, which is valuable to workers on plant materials, but is unsuited for abstraction.

Manures and Manuring.

Attention is still chiefly fixed on the two new fertilisers obtained by the fixation of atmospheric nitrogen—calcium cyanamide and calcium nitrate, both of which are now becoming regular articles of commerce. A new arc for the more economic production of nitric oxide was brilliantly demonstrated at one of the London meetings of the International Congress of Applied Chemistry, and this modification is to be operated by the present producers of calcium nitrate. As regards the fertilisers themselves, little that is novel can be gathered from the reports of the very large number of experiments that have been made with them; calcium nitrate generally proves to be as effective as sodium nitrate—nitrogen for nitrogen—whilst cyanamide falls more into line with ammonium sulphate. Some discussion still goes on as to the exact nature of

³⁶ *Compt. rend.*, 1909, **149**, 91; *A.*, ii, 823.

³⁷ *Zeitsch. physiol. Chem.*, 1909, **61**, 279; *A.*, ii, 824.

the decomposition experienced by calcium cyanamide in the soil, whilst rather contradictory results are reported as to its action on seedlings and young plants. For example, A. Müntz and P. Nottin³⁸ find no bad results even when the cyanamide is sown with the seed or applied as a top dressing, whereas H. von Feilitzen³⁹ observed injurious effects when the fertiliser and seed were sown at the same time, but not when seeding took place a fortnight after sowing the manure. Von Feilitzen sets down the injurious action to calcium carbide contained in the cyanamide, an impurity which has latterly been removed before the fertiliser is sold. Müntz and Nottin found in a series of pot experiments that the cyanamide nitrifies almost as rapidly as ammonium sulphate, although with large quantities there is some delay in starting the action.

Among phosphatic fertilisers, C. G. T. Morison⁴⁰ has been studying the amount of free lime in basic slag, and found, instead of the large amount usually expected, only from 5.29 down to 1.28 per cent. in the samples he examined. After trying various methods for the estimation of the free lime, the author obtained the best results by extracting the finely ground slag with cold water free from carbon dioxide, and titrating the extract.

J. Hendrick⁴¹ has also made a number of determinations of the lime in basic slag by extraction with water, a solution of sugar, and a solution of ammonium chloride respectively. Extraction with water yielded the lowest results, ranging from 0.5 to 2 per cent. in the freshly ground samples examined. Hendrick also showed that the slags contain 15 to 20 per cent. of lime so loosely combined that it will liberate ammonia when distilled with a solution of ammonium sulphate. Probably the basic slag made in the earlier years of the industry contained a greater proportion of free lime, just as it was generally less rich in phosphoric acid.

Morison also discusses the nature of the phosphoric acid compound in basic slag, and from analyses of the crystals obtained from unground cinder, and from the solubility of the slag and of the crystals in weak solvents, he concludes that the compound is $(\text{CaO})_5\text{FeO}\cdot\text{P}_2\text{O}_5\cdot\text{SiO}_2$, instead of the $(\text{CaO})_4\cdot\text{P}_2\text{O}_5$ usually described. This agrees with some previously published analyses of Stead, who also failed to find crystals of tetrabasic phosphate of lime in most of the slags he examined. The compound in question forms pale green or blue needle-shaped crystals in the cinder.

S. U. Pickering⁴² has continued his studies of fungicides and

³⁸ *Compt. rend.*, 1908, **147**, 902; *A.*, ii, 88.

³⁹ *Deut. landw. Presse*, 1909, **36**, 327; *A.*, ii, 430.

⁴⁰ *J. Agric. Sci.*, 1909, **3**, 161.

⁴¹ *J. Soc. Chem. Ind.*, 1909, **28**, 775.

⁴² *J. Agric. Sci.*, 1909, **3**, 171.

similar substances, and has succeeded in clearing up the mysteries which have long clung about the substance known as "Bordeaux mixture," mysteries due to theoretical discussions based on insufficient knowledge or imperfect analyses. The author has already shown⁴³ that with an excess of lime, as used in the ordinary recipe for Bordeaux mixture, a precipitate of the composition $10\text{CuO}\cdot\text{SO}_3$ is formed, whereas when a strictly limited amount of lime is added to the copper sulphate solution, by employing lime-water instead of milk of lime, the compound $4\text{CuO}\cdot\text{SO}_3$ can be obtained. The fungicidal action of Bordeaux mixture is due to the gradual liberation of copper sulphate by the action of atmospheric carbon dioxide on the basic salt, and Pickering shows that carbon dioxide may liberate 25 per cent. of the copper from the latter salt, but only 10 per cent. from the former. He found that secondary reactions increase the quantity of soluble copper up to 40 per cent. of the copper in the salt precipitated by lime-water, and about 25 per cent. of the copper in the ordinary basic salt, but the latter amount is not attained in practice because of the protective action of the lime which is also present alongside. As the lime has also to be carbonated before the copper salt is attacked, it has a further injurious effect by delaying the action of the fungicide. Finally, the calcium carbonate produced has its own precipitating action on the copper salt, so that the fungicidal power of the salt precipitated by lime-water is altogether about twelve times greater than that of the same amount of copper in ordinary Bordeaux mixture; it is also much speedier in action.

A new method of estimating nitrates is described by A. Kleiber,⁴⁴ in which stannous chloride is employed to reduce the nitrate to the state of ammonia; 0.5 gram of the nitrate is placed in a 750—1000 c.c. flask with 5 grams of stannous chloride, 4 to 5 grams of iron filings, 15 c.c. of strong hydrochloric acid, and 7.5 c.c. of water, the mixture being digested for a quarter of an hour on the water-bath.

Chemistry of Animal Nutrition.

In this subject work continues to be very active on the part of the pure physiologists; eventually their work will be applied to agricultural problems, but until the whole question of protein hydrolysis and re-formation in the body has been cleared up no great advance is likely to be made in the feeding of animals on scientific principles.

The evidence as to the specific character of the proteins of each animal that had already been obtained from the experiments of

⁴³ *Trans.*, 1907, **91**, 1988.

⁴⁴ *Chem. Zeit.*, 1909, **33**, 479; *A.*, ii, 517.

Miss Willcock and Hopkins⁴⁵ has been strengthened by further work reported this year. V. Henriques,⁴⁶ experimenting with rats, found that nitrogen equilibrium could not be maintained when zein was the only nitrogen compound fed, although the loss of body-nitrogen was less than on an entirely nitrogen-free diet. Gliadin, which contains tryptophan but not lysine, maintains nitrogen equilibrium, and can even lead to storage of nitrogen. E. Abderhalden⁴⁷ also fed dogs on the cleavage products of casein from which the *l*-tryptophan had been removed. Thereupon they lost body-nitrogen, but the equilibrium was maintained when either the unaltered cleavage products were fed or tryptophan was separately added. While all these papers point to the necessity of the tryptophan group in building up the proteins contained in the organism, they go further, and show that no complete understanding of the peculiarities of animal nutrition is possible until we have a full record of the syntheses of both animal and vegetable proteins. On this latter point Osborne, Leavenworth, and Brantleht⁴⁸ rather abandon the hope of determining the monoamino-acids accurately, and would differentiate the proteins by separating the hexone bases, which can be obtained quantitatively. They give results for about twenty-four vegetable proteins; histidine was present in all to the extent of about 2.5 per cent., lysine was absent from the gliadins but present in the proteins from leguminous seeds. Arginine varied from 1 to 14 per cent., being least in oil seeds, but most abundant in cereals.

The discussion continues of the part played by non-protein nitrogen compounds in nutrition. Morgen, Beger, and Westhausser⁴⁹ fed milch cows on diets in which the non-protein compounds of malt, extract of grass, asparagine, ammonium acetate and tartrate were compared with protein. The authors conclude that the conversion of these substances into digestible proteins in the intestine by the action of bacteria can hardly be regarded as proved. Although of much less value than proteins, they will do some of the work of the latter bodies, not so much by enabling the proteins to be better utilised, as by themselves carrying out some of their functions, although they are probably not converted into materials available for the making of meat or flesh. W. Thaer⁵⁰ fed sheep with hay and various quantities of protein, asparagine, molasses, etc., and found that the nitrogen of the molasses was but little

⁴⁵ *Ann. Report*, 1907, 276.

⁴⁶ *Zeitsch. physiol. Chem.*, 1909, **60**, 105; *A.*, ii, 594.

⁴⁷ *Ibid.*, **61**, 194; *A.*, ii, 327, 817.

⁴⁸ *Amer. J. Physiol.*, 1908, **23**, 180; *A.*, i, 72.

⁴⁹ *Landw. Versuchs-Stat.*, 1909, **71**, 1.

⁵⁰ *Ibid.*, **70**, 413; *A.*, ii, 608.

utilised, the asparagine somewhat more so. The inorganic elements of nutrition have attracted more attention than usual, especially the phosphorus compounds. Hart, McCollum, and Fuller⁵¹ find that animals become unhealthy when the phosphorus in the ration falls below a certain limit; increased amounts result in larger skeletal growth. Nuclein, lecithin, and phytin gave no better results than inorganic phosphates, although there was no evidence of synthesis in the body of organic from inorganic phosphorus compounds. E. Koch,⁵² on the contrary, found that inorganic and non-protein phosphorus compounds are not utilised in repairing phosphorus waste, except perhaps when phosphorus starvation was setting in. From the practical point of view, H. Ingle⁵³ shows that most of the foods, such as oat hay, mealies, and bran, used for horses in South Africa are deficient in lime rather than in phosphoric acid, and possess a very low $\text{CaO}, \text{P}_2\text{O}_5$ ratio. The author connects this badly balanced diet with the prevalence of a disease, osteoperosis, characterised by an exceptional weakening of the bones, which causes considerable mortality in parts of the colony. Ingle recommends the use of leguminous fodders, such as lucerne hay, to provide a greater amount of lime in the diet, instead of the bone meal which is often employed, because in the latter the lime is already combined with phosphoric acid. Certain pastures and particular parts of the country have always been famous for raising horses with good bone, but there has been no scientific investigation of the causes.

A. D. HALL.

⁵¹ *Amer. J. Physiol.*, 1909, **23**, 246; *A.*, ii, 161.

⁵² *St. Petersburg. Med. Woch.*, 1906, 400; *A.*, ii, 162.

⁵³ *J. Agric. Sci.* 1909, **3**, 22.

MINERALOGICAL CHEMISTRY.

IN the two years which have elapsed since the publication of the Report on the Progress of Mineralogical Chemistry during 1907, a great deal of work has been done, much of it of a highly specialised character. An attempt will now be made to classify it under the headings employed in previous issues of this Report, special stress being laid on investigations of general interest.

General and Physical Chemistry of Minerals.

Mineral Gels.—A great deal of attention has of late been paid to the investigation of the colloidal substances which may be conveniently termed gels. Thus H. Stremme¹ has studied artificial precipitates of alumina and silica, and has come to the conclusion that the natural amorphous "hydrated silicates," such as allophane, halloysite, and montmorillonite, are to be regarded, not as definite compounds, but as mixtures of gels of alumina and silicic acid. This suggestion has been followed up by F. Cornu,² who has attempted a classification of such substances found in Nature under the headings: hydroxide gels, carbonate, sulphate, molybdate, uranate, phosphate, arsenate, and antimonate gels, silicate gels, and organic gels. The silicate gels can be further subdivided into groups, such as the chrysocolla group, the gymnite group, etc. Cornu sees in gels the typical products of the normal products of weathering. He points out that it is useless to attempt to give definite chemical formulæ to such substances, and he thinks it probable that many amorphous minerals to which names and formulæ have been assigned will, in the future, prove to be mixtures. It is, however, to be noted that the compositions of many gels agree fairly closely with those of the corresponding crystalline substances.

Hydrated Silicates.—F. Zambonini³ has continued his researches into the part played by water in a number of crystalline hydrated silicates. His experiments have led him to give the formula

¹ *Centr. Min.*, 1908, 622, 661.

² *Ibid.*, 1909, 324; *Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 15, 187; *A.*, 1909, ii, 222, 409.

³ *Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 148; *A.*, ii, 154.

$\text{Zn}_2(\text{ZnOH})_2\text{Si}_2\text{O}_7, \text{H}_2\text{O}$ to hemimorphite. Pyrosmalite he regards as a metasilicate, $(\text{SiO}_3)_2[\text{R}(\text{OH}), \text{Cl}]_4\text{H}_2$. Thaumassite is $\text{CaSiO}_3, \text{CaCO}_3, \text{CaSO}_4, 15\text{H}_2\text{O}$. Cordierite and catapleite do not contain any water of constitution, while sepiolite is derived from an acid, $\text{H}_4\text{Si}_3\text{O}_8$, and has the formula $\text{Mg}_2\text{Si}_3\text{O}_8, n\text{H}_2\text{O}$.

Mutual Relations of Fused Silicates.—In the Report for 1906 an account was given of the exceedingly valuable investigations of the compounds of lime and magnesia with silica made in the Geophysical Laboratory at Washington. This work has since been extended to mixtures containing all three components,⁴ and the study of the compounds of alumina with silica, lime, and magnesia has also been begun.⁵ Both sets of investigations have led to results of the greatest interest and importance. In the first place, it has been shown that CaSiO_3 and MgSiO_3 both exhibit enantiotropy. The α -form of the former, pseudo-wollastonite, is unknown in Nature. The β -form is wollastonite, and inversion takes place about 1190° . The β -form of MgSiO_3 occurs in meteorites. At about 1365° it changes into an ortho-rhombic form distinct from enstatite, and unknown in Nature. The two silicates form but one stable compound, $\text{CaSiO}_3, \text{MgSiO}_3$, identical with diopside. It melts at 1380° , and good crystals can be got from molten calcium chloride. A eutectic occurs between diopside and pseudo-wollastonite, containing about 60 per cent. of the former, and melting at 1348° . A second eutectic, containing 68 per cent. of magnesium silicate, has also been observed. Six solid solutions appear in the system, but only two contain more than a small quantity of the minor component. These are a solution of diopside, to the extent of 17 per cent., in wollastonite, and a solution of magnesium silicate in diopside, the latter taking up about 60 per cent. of its own weight of MgSiO_3 . The study of the alumina-silica series has shown that there is but one compound, Al_2SiO_5 , stable in contact with the melt. This is sillimanite (fibrolite). Andalusite and cyanite change into sillimanite when heated above 1300° . Magnesia also forms but one compound with alumina, namely, $\text{MgO}, \text{Al}_2\text{O}_3$. Lime, on the other hand, forms four compounds with alumina, namely, $3\text{CaO}, \text{Al}_2\text{O}_3$; $5\text{CaO}, 3\text{Al}_2\text{O}_3$, melting at 1387° ; $\text{CaO}, \text{Al}_2\text{O}_3$, melting at 1587° ; and $3\text{CaO}, 5\text{Al}_2\text{O}_3$. The first and the last have no true melting point. The two compounds $5\text{CaO}, 3\text{Al}_2\text{O}_3$ and $3\text{CaO}, 5\text{Al}_2\text{O}_3$ have an unstable form each, while $3\text{CaO}, \text{Al}_2\text{O}_3$ and probably $3\text{CaO}, 5\text{Al}_2\text{O}_3$ are unstable at the melting point. A study of the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is in progress.

The problems presented by the diopside ($\text{CaMgSi}_2\text{O}_6$)-hedenbergite

⁴ E. T. Allen and W. P. White, with optical study by F. E. Wright and E. S. Larsen, *Amer. J. Sci.*, 1909, [iv], **27**, 1; *A.*, ii, 247.

⁵ E. S. Shepherd and G. A. Rankin, *ibid.*, **28**, 293; *A.*, ii, 1015.

($\text{CaFeSi}_2\text{O}_6$) series of minerals have also been attacked in a somewhat different manner by V. Pöschl.⁶ Hedenbergite, chalybite, magnesia, calcium carbonate, and silica were melted together in different proportions. The physical properties of the products, with the exception of the density, were found to vary continuously with the composition. Enstatite and diopside form an isodimorphous series. Somewhat similar results were obtained in the olivine group. A good deal of similar work has also been undertaken by other members of Doelter's school. Mixtures of oligoclase with enstatite or augite have been examined by M. Schmidt.⁷ The freezing-point curves of mixtures of nepheline with ægirite or labradorite and of labradorite with diopside have been plotted by E. Dittler,⁸ and the order of separation in these cases found to be in harmony with Rosenbusch's rule, while mixtures of eläolite and anorthite, as well as those of augite, with labradorite and olivine or magnetite have been studied by H. Schleimer.⁹

Synthetical studies of the potassium alumino-silicates have been made by Z. Weyberg,¹⁰ who has prepared crystalline compounds of the formulæ $\text{K}_2\text{Al}_2\text{SiO}_6$ and $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ respectively. Attempts to obtain similar compounds containing chromium were unsuccessful.

Constitution of Silicates.—In order to throw light on the constitution of the natural silicates, Tschermak decomposes pure material with hydrochloric acid at low temperatures, and, after washing the silicic acid set free, allows it to dry in the air. At first, evaporation of the excess of water alone takes place, but at a certain stage of the process dehydration of the acid begins. This point is determined by weighing the gel of silicic acid at frequent intervals; when the losses corresponding with equal intervals of time are plotted, the point where dehydration of the acid begins is shown by a discontinuity in the curve. By igniting the gel, the composition corresponding with the point of discontinuity can be ascertained, and the particular silicic acid determined of which the mineral under investigation is taken to be the salt. This method has been subjected to adverse criticism by van Bemmelen¹¹ and by O. Mügge.¹² The latter takes objection to it on the grounds (1) that Tschermak's results can in many cases be satisfied by more than one acid; (2) that the point of discontinuity of the curve is largely dependent on the temperature at which drying takes place;

⁶ *Tsch. Min. Mitt.*, 1908, **26**, 413; *A.*, 1908, ii, 400.

⁷ *Jahrb. Min. Beil.-Bd.*, 1909, **27**, 604; *A.*, ii, 590.

⁸ *Monatsh.*, 1908, **29**, 1037; *A.*, ii, 47. ⁹ *Jahrb. Min.*, 1908, ii, 1.

¹⁰ *Centr. Min.*, 1908, 326, 395, 519; *A.*, 1908, ii, 697, 857.

¹¹ *Zeitsch. anorg. Chem.*, 1908, **59**, 225; 1909, **62**, 1; *A.*, 1908, ii, 838; 1909, ii, 234.

¹² *Centr. Min.*, 1908, 129, 325; *A.*, 1908, ii, 277, 688.

(3) that it is uncertain whether the acid set free from the mineral is really the acid of which the mineral is the salt, especially in those cases in which the temperature of decomposition is high; (4) that doubt exists as to how far the acid set free remains stable during the conditions of drying. He supports this criticism by observations made on the gel prepared from natrolite. In reply, Tschermak¹³ states that his method rests on two hypotheses: first, that the acid set free is the acid from which the salt is derived, and, second, that the process of drying takes place in two distinct stages—evaporation of excess of water, followed by dehydration of the acid. These hypotheses may safely be regarded as tenable until facts contradictory of them are recorded. Up to the present this has not been the case. Any apparent ambiguity which arises in interpreting the results can quickly be resolved by considering the empirical formula of the mineral from which the acid is obtained, when one of two or three possible acids will be seen to be much the more probable. Thus, in the case of the acid made from albite, the water percentage is consistent with any one of the following formulæ: $\text{H}_4\text{Si}_5\text{O}_{12}$, $\text{H}_6\text{Si}_8\text{O}_{18}$, $\text{H}_8\text{Si}_{11}\text{O}_{26}$, or $\text{H}_2\text{Si}_3\text{O}_7$. Consideration of the empirical formula of albite, $\text{NaAlSi}_3\text{O}_8$, shows that $\text{H}_2\text{Si}_3\text{O}_7$ ($\text{H}_4\text{Si}_3\text{O}_8 - \text{H}_2\text{O}$) is much the most probable.

Colour of Minerals.—The cause of the often brilliant colours exhibited by natural crystals of substances, which in the pure state are colourless, has given rise of late to a great deal of discussion. There appears to be a general consensus of opinion that the colouring matter, whatever it may be, is present in solid solution, but as to its exact nature widely different opinions have been held. On the one hand, we find those who think that the colour is due to small quantities of organic matter contained in the crystals. They base their belief mainly on the ease with which heat often destroys the colour, and on the fact that small quantities of organic matter or of carbon dioxide and water are given off when the substances are heated in air. On the other hand, we find those who admit no connexion between colour and the presence of organic matter, but believe in the inorganic nature of the pigment. Since the colouring matter appears in many cases to form but a small fraction of a per cent. of the substance, it is at best very difficult, and often quite impossible, to get satisfactory chemical evidence of its existence. And in our present state of knowledge it is easier to speculate on the cause of the phenomena than to give any convincing explanation of the facts observed. A useful summary of the literature of the subject has been recently published by K. Simon,¹⁴ and on the experimental side he has

¹³ *Centr. Min.*, 1908, 225; *A.*, 1908, ii, 490; *Zeitsch. anorg. Chem.*, 1909, **63**, 230; *A.*, ii, 884.

¹⁴ *Jahrb. Min. Beil.-Bd.*, 1908, **26**, 249; *A.*, 1908, ii, 954.

tried the effect of heating amethyst, smoky quartz, tourmaline, topaz, and zircon in hydrogen and oxygen gases. He finds that the colour, which disappears on heating, can often be restored by exposing the minerals to radium radiations or even to direct sunlight. He declares for the inorganic origin of the pigments, but admits that their nature is as yet unknown. Experiments of a somewhat similar kind have been made by W. Hermann,¹⁵ who heated borax glasses, coloured by various oxides, under the same conditions for comparison. The results indicate that the colours of zircon, corundum, spinel, epidote, and beryl are due to oxide of iron, while chromium and manganese, with iron, cause coloration in green zircon, garnet, and tourmaline. In other cases the presence of organic matter introduces complications. Similar conclusions as to the importance of iron, chromium, and manganese as colouring agents have been reached by C. Doelter from an extensive study of the action of radium radiations and of Röntgen and ultra-violet rays on minerals.¹⁶ Experiments on the action of radium in changing the colours of minerals have also been conducted by D. Berthelot,¹⁷ F. Bordas,¹⁸ S. Meyer,¹⁹ and R. Brauns,²⁰ while O. Mügge²¹ has paid special attention to the curious phenomena known as pleochroic halos. No individual case offers greater difficulties, or has been more discussed, than that of rock salt.²² Among the many conflicting views as to the nature of the deep blue colour, that which regards it as due to metallic sodium has met with increasing recognition of late,²³ owing mainly to the work of Siedentopf. It has, however, been justly pointed out that, although fragments of salt can be coloured blue by exposure to sodium vapour, yet such fragments possess very different properties to those of the natural mineral.²⁴ The colour of the latter can be destroyed at a temperature of 275°, while the former remain blue at 400°.

Mineral Analyses.

Apart altogether from assays of ores and of minerals of economic importance made for purely technical purposes, a very large number of complete analyses of minerals of all kinds have been published

¹⁵ *Zeitsch. anorg. Chem.*, 1908, **60**, 369; *A.*, ii, 56.

¹⁶ *Monatsh.*, 1908, **29**, 1145; 1909, **30**, 179; *Zeitsch. Chem. Ind. Kolloide*, 1909, **4**, 188; *A.*, ii, 109, 363, 409; *Centr. Min.*, 1909, 232.

¹⁷ *Compt. rend.*, 1907, **145**, 818; *A.*, 1908, ii, 8.

¹⁸ *Ibid.*, 800, 874; *A.*, 1908, ii, 8, 9.

¹⁹ *Physikal. Zeitsch.*, 1909, **10**, 483; *A.*, ii, 716.

²⁰ *Centr. Min.*, 1909, 721.

²¹ *Ibid.*, 65, 113, 142.

²² See *Ann. Report*, 1906, 324.

²³ F. Cornu, *Centr. Min.*, 1909, 336.

²⁴ G. Spezia, *ibid.*, 398; *A.*, ii, 675.

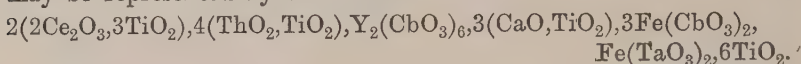
during the past two years. In the space at our disposal it is impossible to refer to them all, even if it were necessary, or desirable, so to do. All that will be attempted, therefore, will be to call attention to those among them which throw light on the composition of rare or imperfectly investigated species, or which have been made with special care on material of which the crystallographic and optical characters have also been determined.

Adamite.—Brilliant ortho-rhombic crystals

$$(a : b : c = 0.9736 : 1 : 0.7013)$$

found in cavities in zinciferous limonite at Monte Valerio, Tuscany, have the formula $\text{Zn}(\text{ZnOH})\text{AsO}_4$.²⁵

Aeschynite.—A specimen from Hitterö has a composition which may be represented by the formula:



The columbic acid obtained from this mineral, and most carefully purified from titanlic and tantalic acids, has properties which suggest that it contains some unknown substance.²⁶

Alstonite.—A very thorough investigation of the properties of this mineral has been made by S. Kreutz,²⁷ who finds that, although the most important constants agree very nearly with those calculated on the supposition that it is an isomorphous mixture of the carbonates of barium and calcium, yet nevertheless undeniable differences exist. The percentage composition of the crystals from Alston Moor was found to be as follows: CaCO_3 , 31.40; BaCO_3 , 62.46; SrCO_3 , 6.05; which may also be expressed as $93.32\text{CaBaC}_2\text{O}_6$, 6.05SrCO_3 , 0.53BaCO_3 . The crystallographic and optical constants of the crystals are: system, ortho-rhombic; $a : b : c = 0.582(7) : 1 : 0.719(5)$. Principal refractive indices for sodium light: $\alpha = 1.5261$, $\beta = 1.671(0)$, $\gamma = 1.671(7)$.

Amphibole Group.—Since the publication two years ago of Penfield and Stanley's highly important work on this complex and difficult group (Annual Report, 1907, p. 289), several valuable papers have appeared. Among these we may notice, in the first place, a long memoir in which S. Kreutz²⁸ gives detailed information as to the optical constants and chemical composition of grünerite from La Mallière, tremolite from Switzerland, actinolite from Zillerthal, richterite from Långban, hornblende from Russell, New York, pargasite from Pargas, and basaltic hornblende from Lukow.

In spite of much careful work, he has only succeeded in tracing

²⁵ P. Aloisi, *Proc. verb. Soc. Toscana Sci. Nat.*, 1907, **17**, 4; *A.*, ii, 587.

²⁶ G. P. Tschernik, *Bull. Acad. Sci. St. Pétersbourg*, 1908, **4**, 389; *A.*, 1908 ii, 399.

²⁷ *Bull. Acad. Sci. Cracow*, 1909, 771.

²⁸ *Sitzungsber. K. Akad. Wiss. Wien.*, 1908, **117**, (i), 877; *A.*, ii, 154.

a connexion between composition and optical properties in the actinolite-tremolite series, where general relations similar to those established by Wülfing for the diopside-hedenbergite series of pyroxenes appear to hold good. In other cases there is no obvious relation between the colour or strength of double refraction and the amount of iron present, and it seems probable that the effect of variation in the amount of certain components, for example, FeO or Al_2O_3 , is not the same in all members of the group. Whence it follows that such components cannot be present as simple silicates, such as FeSiO_3 or $\text{Al}_2\text{Si}_3\text{O}_9$. There is, however, a connexion between absorption and dispersion, the latter increasing rapidly in the neighbourhood of the region of absorption. Another important investigation is due to Washington and Wright,²⁹ who have compared the composition of a black basaltic amphibole from the island of Linosa with that of a very similar mineral described from Greenland under the name kaersutite. Both minerals are highly titaniferous, the chief difference between them being that in the Linosa amphibole, iron is present mainly in the ferric condition, whereas in the specimen from Kaersut, ferrous iron predominates. The proper interpretation of the analytical results is doubtful, but they appear to be consistent with the metasilicate formula of Penfield and Stanley. This formula is also in harmony with the results of an analysis of actinolite from Rhode Island.³⁰ On the other hand, a careful investigation³¹ of a variety of glaucophane, known as rhodusite, in which alumina is nearly completely replaced by ferric oxide, leads to the conclusion that this substance is to be regarded as an isomorphous mixture of the two molecules, $\text{Na}_2\text{Fe}_2\text{Si}_4\text{O}_{12}$ and $(\text{Mg}, \text{Fe}, \text{H}_2, \text{Ca}, \text{Mn})\text{SiO}_3$, in the ratio 1 to 5, a result not in keeping with the formula proposed by Penfield and Stanley. The rhodusite examined came from the neighbourhood of the Asskys River in the Minussinsk district, Siberia, and consisted of greyish-blue, strongly pleochroic fibres. The optical constants and composition of hornblendes from the island of Coll, Hebrides, and from Chester (Mass.) have been determined by Duparc and Pearce.³²

Apophyllite.—An elaborate study of the crystals found in geodes in Melaphyr on the lower Tersja, a tributary of the Tomj river, has been made by Pilipenko.³³ The composition is as follows:

SiO_2 .	Fe_2O_3 .	CaO .	K_2O .	F.	N.	H_2O .	Total.
52.12	0.26	24.56	5.23	1.73	0.02	16.63	100.55

²⁹ *Amer. J. Sci.*, 1908, [iv], **26**, 187; *A.*, 1908, ii, 863.

³⁰ B. L. Johnson and C. H. Warren, *ibid.*, **25**, 1; *A.*, 1908, ii, 202.

³¹ W. Isküll, *Zeitsch. Kryst. Min.*, 1908, **44**, 370; *A.*, 1908, ii, 401.

³² *Bull. Soc. Franç. Min.*, 1908, **31**, 116; *A.*, ii, 60.

³³ *Ann. Géol. Min. Russ.*, 1908, **10**, 200.

Dehydration follows the same course as observed by Hersch.

Argyrodite.—Analyses of material found in the Werner collection at Freiberg³⁴ and of a specimen from Bolivia³⁵ both support the formula, Ag_8GeS_6 , proposed by Penfield. It has been suggested that this may be written in the form $3\text{R}_2^{\text{IS}}, \text{R}_2^{\text{IR}^{\text{IV}}}\text{S}_3$ to bring out an analogy with the formula $3\text{R}_2^{\text{IS}}, \text{R}^{\text{III}}\text{R}^{\text{III}}\text{S}_3$ of tetrahydrite.

Bauxite.—A great many specimens have been analysed by H. Arsandaux,³⁶ who finds that on heating the mineral with strong hydrochloric acid on the water-bath, all the iron is extracted, while nearly the whole of the alumina remains in the insoluble residue. Examination of the residue leads to the conclusion that the amount of water associated with the alumina is independent of the amount of iron present, and may be expressed approximately by the formula $\text{Al}_2\text{O}_3, \text{H}_2\text{O}$. Analyses of this mineral have also been published by R. Lachman,³⁷ and the theory of its formation discussed.

Bertrandite.—Crystals from the Altai Mountains have been examined by Pilipenko.^{37A} Their composition agrees fairly well with the formula $\text{H}_2\text{Gf}_4\text{Si}_2\text{O}_9$.

Brostenite.—This name was applied by P. Poni in 1900 to certain manganites of manganese and ferrous iron of variable composition occurring in crystalline schists near Brosteni, in Roumania. These deposits have recently been the subject of detailed study by V. C. Butureanu.³⁸ He concludes that the brostenites are the result of the oxidation of a carbonate of composition $5\text{MnCO}_3, \text{FeCO}_3$, and belong to the four following types: $\text{RO}, 2\text{MnO}_2, 2\text{H}_2\text{O}$; $\text{RO}, 3\text{MnO}_2, 2\text{H}_2\text{O}$; $\text{RO}, 3\text{MnO}_2, 3\text{H}_2\text{O}$; and $\text{RO}, 5\text{MnO}_2, \text{H}_2\text{O}$.

The manganese ore of the Queluz district, Brazil, appears to have had a somewhat similar origin, for O. A. Derby³⁹ finds that it has been derived from a rock consisting largely of manganese carbonate, his first impression that it was derived from the weathering of a rock rich in manganese garnet having proved incorrect. The manganese deposits of India have been exhaustively studied by L. L. Fermor,⁴⁰ who has embodied his results in an elaborate memoir. He has observed several new minerals in these deposits (see juddite, sitaparite, and vredenburgite).

Carlosite.—The substance to which this name was given was found accompanying benitoite in California, and was at first believed to

³⁴ F. Kolbeck, *Centr. Min.*, 1908, 331; *A.*, 1908, ii, 703.

³⁵ V. M. Goldschmidt, *Zeitsch. Kryst. Min.*, 1908, 45, 548; *A.*, ii, 58.

³⁶ *Compt. rend.*, 1909, 148, 936, 1115; *A.*, ii, 490, 587.

³⁷ *Zeitsch. prakt. Geol.*, 1908, 16, 353.

^{37A} *Bull. Acad. Sci. St. Pétersbourg*, 1909, 1116; *A.*, 1910, ii, 48.

³⁸ *Ann. Sci. Univ. Jassy*, 1908, 5, 87; 1909, 6, 7; *A.*, 1908, ii, 955; 1909, ii, 745.

³⁹ *Amer. J. Sci.*, 1908, [iv], 25, 213; *A.*, 1908, ii, 506.

⁴⁰ *Mem. Geol. Surv. India*, 1909, 37, pp. 1—610.

be a new mineral. It has proved, however, on further examination to be identical with neptunite.⁴¹ In composition the material from California is very similar to that from Greenland, but rather less manganese and more calcium and magnesium are present in the former. The formula is $R_2^I R_2^{II} Ti Si_4 O_{12}$, where $R^I = Na$ and K , and $R^{II} = Fe, Ca, Mg, \text{ and } Mn$.

Chlormanganokalite.—A new analysis agrees approximately with the formula $4KCl, MnCl_2$.⁴² The mineral is rhombohedral ($a : c = 1 : 0.5801$), not monoclinic as stated by Lacroix. The crystals are pale yellow, highly deliquescent rhombohedra. The index of refraction is about 1.59, and the birefringence very low. A good uniaxial interference figure was observed in a section cut perpendicular to the trigonal axis of the rhombohedron.

Chlornatrokalite.—Further investigation has shown this substance to be merely an intimate mixture of the chlorides of potassium and sodium.⁴³

Conichalcite.—Minute indistinct crystals of this rare mineral have been found lining cavities in copper ore at Maya-Tass, in the Province of Akmolinsk, Western Siberia.⁴⁴ The optical characters point to ortho-rhombic symmetry. The composition is as follows:

As_2O_5 .	P_2O_5 .	CuO .	CaO .	Fe_2O_3 .	MgO .	H_2O .	Total.
36.40	1.30	31.55	23.10	0.40	1.90	5.15	99.80

Connellite.—Our knowledge of the composition of this very rare mineral has depended hitherto on an analysis made by Penfield of a very small quantity. The recent discovery of a specimen at Bisbee, Arizona, has enabled C. Palache and H. E. Merwin⁴⁵ to make a fresh examination of the substance. They conclude that the formula is $Cu_{22}Cl_4SO_{23} \cdot 20H_2O$, a result which differs considerably from Penfield's formula $Cu_{15}(Cl, OH)_4SO_{16} \cdot 15H_2O$.

Coronadite.—L. L. Fermor⁴⁶ has pointed out that this mineral may be regarded as a salt of the same hypothetical acid, H_4MnO_5 , from which hollandite and psilomelane are derived, and assigns to it the formula $Mn_{21}Pb_6R_5^{II}(MnO_5)_{16}$.

Cossyrite.—This mineral is a variety of ænigmatite, found in small crystals weathered out of the pantellerite of the island of Pantelleria. It has recently been the subject of an exhaustive study by J. Soellner.⁴⁷ The symmetry is anorthic, and the constants

⁴¹ W. M. Bradley, *Amer. J. Sci.*, 1909, [iv], **28**, 15; *A.*, ii, 815.

⁴² H. J. Johnston-Lavis and L. J. Spencer, *Min. Mag.*, 1908, **15**, 54; *A.*, 1908, ii, 395.

⁴³ *Ibid.*

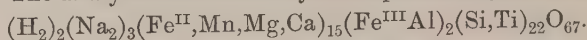
⁴⁴ L. Michel, *Bull. Soc. franç. Min.*, 1909, **32**, 50; *A.*, ii, 491.

⁴⁵ *Amer. J. Sci.*, 1909, [iv], **28**, 537; *A.*, 1910, ii, 47.

⁴⁶ *Rec. Geol. Surv. India*, 1908, **36**, 295; *A.*, ii, 153.

⁴⁷ *Zeitsch. Kryst. Min.*, 1909, **46**, 518; *A.*, ii, 814.

as follows: $a : b : c = 0.66856 : 1 : 0.35173$; $\alpha = 90^\circ 4\frac{3}{4}'$, $\beta = 102^\circ 30'$, $\gamma = 90^\circ 18\frac{1}{2}'$. The angle between the good cleavages, $110 : 1\bar{1}0$, is $66^\circ 16'$. The analytical results may be expressed by the formula



It is pointed out that cossyrite, ænigmatite, and rhönite may be regarded as a group of isomorphous minerals intermediate between the pyroxenes and the amphiboles.

Cryolite.—F. Cornu⁴⁸ has suggested that the change of system which Nacken has observed to take place between 550° and 570° is due to the formation of a cubic substance isomorphous with cryolithionite.

Danburite.—Rough, corroded crystals from Maharitra, Madagascar, have been shown to possess the ordinary formula, $\text{CaO}, \text{B}_2\text{O}_3, 2\text{SiO}_2$.⁴⁹

Dysanalyte.—The small, iron-black crystals found in the granular limestone from the neighbourhood of Vogtsburg (Kaiserstuhl i/Br) were for long regarded as perowskite, but since A. Knop detected in them considerable quantities of columbium and cæsium, they have been considered as constituting a separate species under the name dysanalyte. The correctness of this conclusion has been challenged by O. Hauser,⁵⁰ who holds that the substance is merely perowskite contaminated by enclosures. Analysis of selected crystals gave the following results:

TiO_2 .	SiO_2 .	Cb_2O_5 .	Ce_2O_3 .	FeO .	CaO .	MnO .	Na_2O .	Total.
50.93	2.21	4.86	2.80	9.22	25.60	0.23	4.37	100.22

Datolite.—The composition of a specimen analysed by J. Fromme⁵¹ agrees very well with the formula $\text{Ca}(\text{BOH})\text{SiO}_4$, if it be assumed that a little of the boron is replaced by aluminium.

Fichtelite.—Crystals from a peat bog at Borkovic, Bohemia, have been shown to belong to the hemimorphic class of the oblique system.⁵² Analysis gave the formula $\text{C}_{18}\text{H}_{32}$, a result confirmed by molecular weight determinations.

Felspar Group.—It has long been known that analyses of the potash felspar *orthoclase*, KAlSi_3O_8 , made on pure, apparently homogeneous material, often show the presence of sodium and sometimes of calcium as well. In explanation it has been assumed that these elements are contained in albite or anorthite, present either in isomorphous or mechanical mixture. The problem offered by such orthoclases has recently received a good deal of attention.

⁴⁸ *Centr. Min.*, 1908, 546; *A.*, 1908, ii, 955.

⁴⁹ A. Lacroix, *Bull. Soc. franç. Min.*, 1908, 31, 315; *A.*, ii, 812.

⁵⁰ *Zeitsch. anorg. Chem.*, 1908, 60, 237; *A.*, ii, 60.

⁵¹ *Tsch. Min. Mitt.*, 1909, 28, 312.

⁵² F. Plzák and V. Rosický, *Zeitsch. Kryst. Min.*, 1908, 44, 332; *A.*, 1908, ii, 395.

The analytical work of Barbier and Prost⁵³ tends to show that sodium is not present as albite, but as a monoclinic sodium silicate isomorphous with orthoclase. A similar conclusion has been reached by Schwantke⁵⁴ as regards calcium, for he attributes its presence to the hypothetical molecule $\text{CaAl}_2\text{Si}_6\text{O}_{16}$. He has pointed out that the existence of stilbite, $(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_6\text{O}_{16}, 6\text{H}_2\text{O}$, lends support to the idea that such a molecule is possible. On this view the intergrowth of plagioclase and quartz, probably derived from alteration of orthoclase and known as myrmekite, can be explained as due to the conversion of $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ into $\text{CaAl}_2\text{Si}_2\text{O}_8$ with separation of silica. The problem has also been attacked by melting together synthetical preparations of orthoclase and anorthite, and of orthoclase and plagioclase.⁵⁵ It has been found that orthoclase is only miscible to a very slight extent with anorthite. With plagioclase the tendency to form mixed crystals is greater, and increases with the amount of albite substance present. In both cases zoned crystals are formed, the centre being rich in calcium, while the edges contain much potassium. Pure orthoclase does not crystallise out of the mixture. This case of mixed crystallisation apparently conforms to type IV of Retgers,⁵⁶ in which the components are isodimorphous, and a considerable gap exists.

The distinction between orthoclase and microcline made by Des Cloizeaux on optical grounds has been the subject of a chemical study by P. Barbier.⁵⁷ He finds that small quantities of lithium or of rubidium or of both these elements invariably occur in orthoclase, but are not found in microcline. In this he sees a fundamental chemical difference between the two minerals, a view in which he is supported by F. Gonnard.⁵⁸ The crystallographic constants of good crystals of pure albite from South Greenland have been determined by Dreyer and Goldschmidt.⁵⁹ Minute crystals of andesine from Monte Palmas, Sardinia, have been shown by F. Millosevich⁶⁰ to possess properties in harmony with a position in the plagioclase series between Ab_2An and Ab_3An_2 . An interesting illustration of the application of the methods of physical chemistry to the study of a rock is to be found in Vogt's paper⁶¹ on a labradorite-norite from the Lofoten Islands.

⁵³ *Bull. Soc. chim.*, 1908, [iv], **3**, 894; *A.*, 1908, ii, 863.

⁵⁴ *Centr. Min.*, 1909, 311; *A.*, ii, 588.

⁵⁵ E. Dittler, *ibid.*, 663.

⁵⁶ *Zeitsch. physikal. Chem.*, 1889, **3**, 552.

⁵⁷ *Compt. rend.*, 1908, **146**, 1330; *A.*, 1908, ii, 704.

⁵⁸ *Bull. Soc. franç. Min.*, 1908, **31**, 303.

⁵⁹ *Meddelelser om Grönland*, 1907, **34**, 1; *A.*, 1908, ii, 116.

⁶⁰ *Atti R. Accad. Lincei*, 1909, [v], **18**, i, 22; *A.*, ii, 248.

⁶¹ *Quart. J. Geol. Soc.*, 1909, **65**, 81; *A.*, ii, 678.

Guarinite.—This species occurs in small, yellow crystals in the sanidine bombs of Monte Somma, and was described in 1857 by Guiscardi as an orthorhombic calcium titano-silicate. Rebuffat subsequently gave it the formula



As a recent examination of the crystals proved them to be anorthic with the angles and optical characters of hiortdahlite, a new analysis was undertaken by G. T. Prior, with the result that the identity with hiortdahlite was completely proved, the formula of the mineral being $3\text{CaSiO}_3, [\text{Ca}(\text{F}, \text{OH})]\text{NaZrO}_3$.⁶²

Gedrite.—Sheaves of long, narrow crystals of this aluminous variety of anthophyllite have been found abundantly in amphibolite in Ontario.⁶³ The mineral has a clove-brown colour, and exhibits characteristic pleochroism. Its composition is very similar to that of a specimen from Gèdres in the Pyrenees, and may be represented by a formula of the type given by Rammelsberg: $4\text{RSiO}_3, \text{Al}_2\text{O}_3$, where $\text{R} = \text{Mg}, \text{Fe}, \text{H}_2$.

Gehlenite occurs as a contact mineral near the junction of altered limestone and intrusive basic diorite in the Velardeña district of Durango, Mexico. Crystals were not observed, but F. E. Wright⁶⁴ was able to establish the identity of the mineral by its physical characters. The substance has a fair basal cleavage, and is uniaxial: $\omega = 1.6$, $\omega - \epsilon = 0.0055$. The composition cannot be expressed by any simple formula, but is similar to that of other specimens from Monzoni, Falkirk, and Clarence, the mineral being essentially a calcium aluminium silicate.

Hatchettite.—A crystalline substance, possessing optical characters suggestive of orthorhombic symmetry, has been found in nests in Cretaceous marl near Cracow.⁶⁵ It appears to be a paraffin of the formula $\text{C}_{38}\text{H}_{78}$.

Hopeite.—The brilliant crystals which occur associated with vanadinite on a bone-breccia in a cavern in the zinc and lead ore at Broken Hill, Rhodesia, are found on optical examination to consist of an intimate interlamination of two modifications which differ in density, optical character, and the rate at which they lose water on heating, but possess the same chemical composition, agreeing with the formula $\text{Zn}_3\text{P}_2\text{O}_8, 4\text{H}_2\text{O}$. L. J. Spencer⁶⁶ proposes to call these two modifications α -hopeite and β -hopeite respec-

⁶² F. Zambonini, *Min. Mag.*, 1909, **15**, 247; *A.*, ii, 677.

⁶³ N. N. Evans and J. A. Bancroft, *Amer. J. Sci.*, 1908, [iv], **25**, 509; *A.*, 1908, ii, 604.

⁶⁴ *Amer. J. Sci.*, 1908, [iv], **26**, 545; *A.*, ii, 62.

⁶⁵ J. A. Morozewicz, *Bull. Acad. Sci. Cracow*, 1908, 1067; *A.*, ii, 409.

⁶⁶ *Min. Mag.*, 1908, **15**, 1; *A.*, 1908, ii, 397.

tively. His observations and conclusions have recently been subjected to some criticism by G. Cesàro.⁶⁷

Hortonolite.—This rare species has been discovered in veins traversing an ultrabasic olivine rock at Rhode Island.⁶⁸ In composition it resembles closely the material from Munroe, Orange Co., N.J., analysed by Penfield and Forbes.

Hydrated Calcium Carbonate.—P. N. Tschirwinsky⁶⁹ has recently reviewed our knowledge of the hydrated forms of calcium carbonate. He regards only three of these as definitely established, namely, $\text{CaCO}_3 \cdot 3\text{H}_2\text{O}$; $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$; and $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$. The first two occur as minerals, and may be termed trihydrocalcite and pentahydrocalcite respectively (compare *Ann. Report*, 1906, 307).

Ilvaite.—A specimen from Elba, examined by Tschermak's method, gave results indicating that it was derived from the diorthosilicic acid, $\text{H}_6\text{Si}_2\text{O}_7$.⁷⁰ The formula is therefore written $(\text{FeO})_2\text{Fe}_2(\text{FeOH})_2(\text{Si}_2\text{O}_7)_2$.

Janosite.—Some time ago R. Scharizer⁷¹ suggested that the mineral janosite asserted by Weinschenk and Toborffy to be identical with copiapite might really be a mixture of copiapite, $\text{Fe}_4\text{S}_5\text{O}_{21} \cdot 18\text{H}_2\text{O}$, with ferric tetrasulphate, $\text{Fe}_2\text{S}_4\text{O}_{15} \cdot 9\text{H}_2\text{O}$. He has since found that fresh experiments support this conclusion. He believes, moreover, that it is necessary to distinguish between ordinary or α -copiapite, $(\text{HO})_2\text{Fe}_4(\text{SO}_4)_5 \cdot 17\text{H}_2\text{O}$, and another similar substance which he calls β -copiapite, $(\text{HO})\text{Fe}_3(\text{SO}_4)_4 \cdot 13\text{H}_2\text{O}$, and which is possibly identical with Rammelsberg's *misy*.

Kaolinite.—The white product resulting from the weathering of quartz-porphry in the neighbourhood of Halle has been analysed by V. Selle,⁷² who has also determined the composition of the portion insoluble in concentrated sulphuric acid. He concludes that mica was the first product of the alteration of the felspar in the rock, and that it was subsequently converted into kaolinite. In the Halle district the decomposed porphyries are richest in kaolinite near the surface, and minerals of pneumatolytic origin are absent. It may therefore be deduced that the formation of kaolinite is dependent on the ordinary processes of weathering.

Kröhnkite.—Large, oblique crystals from Chili have been examined by Palache and Warren.^{7A} They have the usual formula $\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$.

⁶⁷ *Bull. Acad. roy. Belg.*, 1909, 567; *A.*, ii, 745.

⁶⁸ B. L. Johnson and C. H. Warren, *Amer. J. Sci.*, 1908, [iv], 25, 35; *A.*, 1908, ii, 202.

⁶⁹ *Zeitsch. Kryst. Min.*, 1909, 46, 302; *A.*, ii, 492.

⁷⁰ E. Baschieri, *Proc. verb. Soc. Toscana Sci. Nat.*, 1907, 16, 49; *A.*, ii, 589.

⁷¹ *Zeitsch. Kryst. Min.*, 1909, 46, 427; *A.*, ii, 587.

⁷² *Zeits. Naturw.*, 1907, 79, 321; *A.*, ii, 63.

^{72a} *Amer. J. Sci.*, 1908, [iv], 26, 342; *A.*, 1908, ii, 1047.

Mangano-tantalite.—Large masses of this mineral have been found in pegmatite-veins in the Wodgina tin-field, Western Australia. A specimen analysed by Simpson was found to contain 68.65 per cent. Ta_2O_5 , 15.11 per cent. Cb_2O_5 , and 14.15 per cent. MnO .⁷³

Meymacite.—Native anhydrous tungstic acid, WO_3 , and a hydrated form, $WO_3 \cdot 2H_2O$, have been described under the names of tungstite and meymacite by Silliman and Carnot respectively. No analysis of Silliman's mineral has been published, and the material examined by Carnot was so impure that the formula assigned to it can only be regarded as uncertain. The study of similar specimens found near Salerno in British Columbia has led Walker⁷⁴ to the conclusion that tungstite and meymacite are identical, and that the true formula for the mineral is $WO_3 \cdot H_2O$. He suggests that the name tungstite should be retained. The material from Salerno has resulted from the alteration of wolframite. As it was not found possible to obtain a pure specimen for analysis by mechanical means, advantage was taken of the solubility of the mineral in ammonia and dilute soda. After deducting insoluble impurities, the results were in harmony with the formula given above.

Mimetite.—Two varieties of this mineral, one yellow and the other white or colourless, are found in the cupriferous strata of Sardinia.⁷⁵ They vary slightly in chlorine content, and exhibit a corresponding variation in the value of the angle $10\bar{1}1:0001$, the numbers being $40^\circ 4'$ for the yellow crystals which contain 2.30 per cent. of chlorine, and $39^\circ 52'$ for the white crystals with 2.44 per cent. of chlorine.

Monazite.—Yellow crystals from Carolina have been analysed by G. P. Tschernik,⁷⁶ and the question of the condition in which thorium exists in the mineral has been discussed by O. Kress and F. J. Metzger.⁷⁷ The thorium has been held to be present as silicate (thorite or orangite), or as phosphate, or in both these forms. To throw light on the problem, Kress and Metzger have determined the percentages of thoria, quartz, silicate silica, and total silica in a very large number of specimens. As they find that in general the silica available for combination with the thoria is in defect, they conclude that the thorium is not present as silicate. This conclusion was confirmed by microscopical examina-

⁷³ A. G. Maitland, *Bull. geol. Survey Western Australia*, **23**, 65; *A.*, ii, 59.

⁷⁴ *Amer. J. Sci.*, 1908, **25**, 305; *A.*, 1908, ii, 507.

⁷⁵ A. Serrì, *Atti R. Accad. Lincei*, 1909, [v], **18**, i, 361; *A.*, ii, 492.

⁷⁶ *Bull. Acad. Sci. St. Pétersbourg*, 1908, 243; *A.*, 1908, ii, 302.

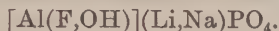
⁷⁷ *J. Amer. Chem. Soc.*, 1909, **31**, 640; *A.*, ii, 588.

tion, which showed that the silicate present in monazite is quite different to thorite, and is very likely a felspar.

Morinite is an alteration product of amblygonite, and occurs in small, oblique crystals with tin-ore at Montebbras (Creuse).⁷⁸ Its composition is represented by the formula



which, expressed in the form $(\text{AlF})_3\text{Na}_2\text{H}(\text{PO}_4)_3, (\text{CaF})_3\text{PO}_4, 8\text{H}_2\text{O}$, shows in the first molecule a relation to amblygonite,



Nepheline.—J. A. Morozewicz⁷⁹ has found that nepheline is completely soluble in *N*/4-hydrochloric acid, and that enclosed impurities may thus be readily separated. Taking advantage of this fact, he has analysed three specimens of elæolite from the Mariupol district, Sea of Azov, an elæolite from Mias, Urals, and two sets of crystals from Vesuvius. In all the ratio $(\text{Al}, \text{Fe})_2\text{O}_3 : (\text{Na}_2, \text{K}_2, \text{Ca})\text{O} = 1 : 1$, but the ratio $(\text{SiTi})\text{O}_2 : (\text{Al}, \text{Fe})_2\text{O}_3$ varies from 2.11 : 1 to 2.21 : 1. The ratio $\text{K}_2\text{O} : (\text{Na}_2\text{O} + \text{CaO})$ varies from 1 : 4.06 to 1 : 5.6, being usually 1 : 4.4. These results, considered in connexion with earlier work, lead to the conclusion that sodium and potassium do not replace one another isomorphously, but that most analyses may be represented as combinations of the molecule $\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ with 4, $4\frac{1}{2}$, 5, or $5\frac{1}{2}$ molecules of $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$.

Nephrite.—Analyses of a series of specimens of New Zealand "greenstone," selected to illustrate the variation of composition with colour, have been published by A. M. Finlayson.⁸⁰

Nontronite.—Pseudomorphs of nontronite after wollastonite are found in the copper mines at Aranzazú, near Concepción del Oro, in Mexico.⁸¹ They have been formed by the action on wollastonite of iron sulphate derived from the alteration of copper pyrites. The formula $\text{H}_8\text{Fe}_4\text{Si}_9\text{O}_{28}$ has been deduced from an analysis of the purified material. This differs considerably from the formula, $\text{H}_4\text{Fe}_2\text{Si}_2\text{O}_9$, proposed by Weinschenk for nontronite from near Passau.

Oncosine is a compact variety of muscovite, which swells up and intumesces when heated. A specimen has recently been analysed by G. Piolti.⁸²

Orihite.—Well-developed crystals from the Radautal have been

⁷⁸ A. Carnot and A. Lacroix, *Bull. Soc. franç. Min.*, 1908, 31, 149; *A.*, ii, 58.

⁷⁹ *Bull. Acad. Sci. Cracow*, 1907, 958; *A.*, 1908, ii, 201.

⁸⁰ *Quart. J. geol. Soc.*, 1909, 65, 351; *A.*, ii, 901.

⁸¹ A. Bergeat, *Centr. Min.*, 1909, 161; *A.*, ii, 411.

⁸² *Atti R. Accad. Sci. Torino*, 1909, 44, 743; *A.*, ii, 813.

measured and analysed by J. Fromme.⁸³ In addition to the usual constituents, the specimen contained small quantities of yttrium and glucinum. A formula of the general type,



expresses the results fairly well. A full account of the analytical methods employed will be found in the original paper.

Paligorskite Group.—A number of somewhat ill-defined minerals, such as "mountain leather," have been grouped together under this name. An elaborate critical discussion of the available data has led A. Fersmann⁸⁴ to divide the group into the seven following classes: (1) paramontmorillite of the general composition $\text{H}_{12}\text{Al}_2\text{Si}_4\text{O}_{17}$; (2) α -paligorskite, $\text{H}_{32}\text{Mg}_2\text{Al}_4\text{Si}_{11}\text{O}_{46}$; (3) β -paligorskite, $\text{H}_{20}\text{Mg}_2\text{Al}_2\text{Si}_7\text{O}_{29}$; (4) α -pilotite, $\text{H}_{28}\text{Mg}_4\text{Al}_2\text{Si}_{10}\text{O}_{41}$; (5) β -pilotite, $\text{H}_{36}\text{Mg}_6\text{Al}_2\text{Si}_{13}\text{O}_{53}$; (6) parasepiolite, $\text{H}_3\text{Mg}_2\text{Si}_3\text{O}_{12}$; (7) ferruginous paligorskite.

Palmierite.—Although the analytical results agree best with the formula $4\text{PbSO}_4, 3[(\text{K}, \text{Na})_2\text{SO}_4]$, there is some reason to believe⁸⁵ that the true formula is $\text{PbSO}_4, (\text{K}, \text{Na})_2\text{SO}_4$.

Peridot.—Good crystals from St. John's Island (Zebirget), in the Red Sea, have been analysed by J. Couyat.⁸⁶ His results are very similar to those recorded by Stromeyer for oriental peridot. The indices of refraction (sodium light) are: $\alpha = 1.6546$; $\beta = 1.6706$; $\gamma = 1.6898$, values which agree closely with those obtained by Zimányi.

Plumosite.—A felted aggregate of dark steel-grey fibres from Felsöbánya has been analysed by J. Loczka.⁸⁷ The material examined appeared to be free from stibnite and iron pyrites. The formula deduced is $4\text{PbS}, \text{FeS}, 3\text{Sb}_2\text{S}_3$, but the results obtained agree best with the formula $7(\text{Pb}_{4/5}, \text{Fe}_{1/5})\text{S}, 4\text{Sb}_2\text{S}_3$, given by Spencer and Prior to jamesonite, of which mineral plumosite is merely a variety.

Pyromorphite.—Crystals from British Columbia have been the subject of careful chemical and crystallographic examination by O. Bowles.⁸⁸ Two varieties are distinguished, which differ in colour and to a slight extent in composition also. A comparative study of specimens from various localities has also been made by R. Brauns.⁸⁹ Dark brown crystals from Ägidienberg of normal composition have been found by him to have the axial ratio $a : c = 1 : 0.72926$.

⁸³ *Tsch. Min. Mitt.*, 1909, **28**, 318.

⁸⁴ *Bull. Acad. Sci. St. Pétersbourg*, 1908, 637; *A.*, 1908, ii, 603.

⁸⁵ A. Lacroix, *Bull. Soc. franç. Min.*, 1908, **31**, 260; *A.*, ii, 57.

⁸⁶ *Bull. Soc. franç. Min.*, 1908, **31**, 344; *A.*, ii, 813.

⁸⁷ *Ann. Musei Nat. Hungarici*, 1908, **6**, 586; *A.*, ii, 153.

⁸⁸ *Amer. J. Sci.*, 1909, [iv], **28**, 40; *A.*, ii, 900.

⁸⁹ *Centr. Min.*, 1909, 257; *A.*, ii, 492.

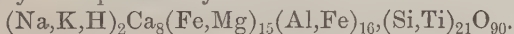
Pyrochlore.—The results of analysis of octahedral crystals from the Caucasus may be expressed⁹⁰ in the form $Y_2O_3, Cb_2O_5 + 2(2CaO, Cb_2O_5), 2Ca(CbO_3)_2, 4Fe(CbO_3)_2, Mg(CbO_3)_2, 2(CaO, TiO_2), 4NaF$.

Quartz.—In 1890 Le Chatelier made the very important and interesting observation that quartz undergoes a reversible change at about 570° . This change is manifested by a sudden alteration in the coefficient of expansion, in the circular polarisation, and in the birefringence. The phenomenon was subsequently investigated from the crystallographic side by O. Mügge,⁹¹ who, from a study of the etched figures, came to the conclusion that the form of quartz stable below 570° , and termed by him α -quartz, belonged to a different type of symmetry to the form stable above 570° , so-called β -quartz. These two forms have recently been the subject of detailed examination by Wright and Larsen,⁹² who place the transition temperature at $575^\circ \pm 2^\circ$. They emphasise the fact, pointed out by Mügge, that quartz which has been heated above 575° possesses properties, notably a peculiar twin structure, which enable it to be distinguished from quartz which has never reached this temperature. On the possibility of this discrimination they base the use of quartz as a kind of "geological thermometer," and discuss its application to the elucidation of the past history of various rocks, their general conclusion being that vein and geode quartzes and certain large pegmatite quartz masses and pegmatite veins were formed below 575° , while graphic and granite pegmatites and granites and porphyry quartzes were in all probability formed above that temperature.

The relations between quartz, chalcedony, and opal have been studied by H. Leitmeier.⁹³ Specimens of the three minerals were heated with a 50 per cent. solution of potassium hydroxide at 80° for five hours, and from their behaviour under these conditions the conclusion was drawn that quartz and chalcedony are varieties of the same species.

Rhodizite.—Our knowledge of the composition of this rare borate has hitherto been confined to an analysis made by Damour. The recent discovery of the mineral in Madagascar has provided material for a fresh investigation.^{93a} The results lead to the formula $6B_2O_3, 3Al_2O_3, 4GfO, 4(Li, K, Na, H)_2O$.

Rhönite.—The composition of large, black crystals analysed by Pisani^{93b} may be expressed by the formula



⁹⁰ G. P. Tschernik, *Bull. Acad. Sci. St. Pétersbourg*, 1909, 365; *A.*, ii, 411.

⁹¹ *Jahrb. Min. Festband*, 1907, 181; *A.*, 1908, ii, 302.

⁹² *Amer. J. Sci.*, 1909, [iv], 27, 421. ⁹³ *Centr. Min.*, 1908, 632; *A.*, 1908, ii, 954.

^{93a} A. Lacroix, *Compt. rend.*, 1909, 149, 896; *A.*, 1910, ii, 46.

^{93b} A. Lacroix, *Bull. Soc. franç. Min.*, 1909, 32, 325; *A.*, 1910, ii, 49.

Reyerite.—A scaly zeolitic mineral from Niakornat, in Greenland, has been identified with reyerite (see *Ann. Report*, 1907, 288) by O. B. Boeggild.⁹⁴ The composition of the rhombohedral crystals may be expressed by the formula $2\text{CaO}, 3\text{SiO}_2, 1\frac{1}{2}\text{H}_2\text{O}$ or $\text{H}_2\text{Ca}_2(\text{SiO}_3)_{3,2}\text{H}_2\text{O}$.

Rutile.—Small crystals from Vaux (Rhône), which were apparently quite free from inclusions, were found to contain 1.75 per cent. of oxide of tin.⁹⁵ This observation is interesting on account of the isomorphous replacement of titanium by tin.

Sassolite.—If steam is passed over tourmaline at a high temperature and then condensed, it is found to contain traces of boric acid. This fact has been adduced by R. Nasini⁹⁶ in support of the theory that sassolite is derived from tourmaline. His views have, however, been criticised by G. D'Achiardi.⁹⁷

Soda Nitre.—The results of analyses of several samples of Chili saltpetre show that all contain iodate, and some, perchlorate.⁹⁸ The samples rich in sodium nitrate contain potassium nitrate as well, and also small amounts of chromate.

Stephanite.—Some remarkably fine crystals from Arizpe, Mexico, have been described by W. E. Ford.⁹⁹ The formula $5\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$ is in good agreement with the analytical results.

Strüverite.—In a detailed account of the analysis of this mineral, Prior¹ has discussed the difficulties which attend the separation of columbic, tantalic, and titanic acids, and has shown that the usual gravimetric methods bring out the percentage of titanium considerably too high. In the light of these results he re-examined the ilmenorutile from the Ilmen Mountains, and from Evje, in Norway, and found, on estimating the titanium colorimetrically, that his view was correct. These determinations, together with two new analyses, of which the first was made on a specimen from the Ilmen Mountains, and the second on one from Iveland in Norway, correspond approximately with the formula $\text{FeO}, \text{Cb}_2\text{O}_5, 5\text{TiO}_2$, with possibly some admixture of FeTiO_3 or FeTi_2O_5 , and thus exhibit analogy to the formula assigned to strüverite, $\text{FeO}(\text{Ta}, \text{Cb})_2\text{O}_5, 4\text{TiO}_2$, a substance of similar crystalline form. His conclusion is that strüverite and ilmenorutile may best be represented as solid solutions of the rutile (TiO, TiO_3) and tapiolite or mossite ($\text{Fe}[(\text{Ta}, \text{Cb})\text{O}_3]_2$) molecules, the former name

⁹⁴ *Meddelelser om Grönland*, 1908, **34**, 93; *A.*, 1908, ii, 399.

⁹⁵ G. Friedel and Grandjean, *Bull. Soc. franç. Min.*, 1909, **32**, 52; *A.*, ii, 491.

⁹⁶ *Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 43; *A.*, 1908, ii, 862.

⁹⁷ *Ibid.*, 238; *A.*, 1908, ii, 955.

⁹⁸ F. W. Dafert, *Monatsh.*, 1908, **29**, 235; *A.*, 1908, ii, 603.

⁹⁹ *Amer. J. Sci.*, 1908, [iv], **25**, 244; *A.*, 1908, ii, 505.

¹ G. T. Prior and F. Zambonini, *Min. Mag.*, 1908, **15**, 78; *A.*, 1908, ii, 398.

being appropriate for those rich in tantalic acid, whilst the latter may be kept for those in which columbic acid predominates.

Vesuvianite.—A number of specimens have been tested for boron by Wherry and Chapin.² The largest amount was found in the crystals from the Wilui river in Siberia. The authors draw attention to the fact that the amount of ferric iron present is always small, never exceeding 5 per cent., and they suggest that this indicates that only part of the aluminium is basic, most of it, together with the boron, playing the part of an acid. To give expression to this view, Clarke's formula for vesuvianite,

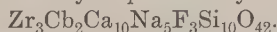


($R^{II} = H_2, K_2, Na_2, Mg, Ca, Fe, Mn$, and also $AlOH$ and AlF with Fe^{III} , Mn^{III} , or B replacing some of the Al), may be written in the form $Ca_7(R^{II}AlO_2)_2(SiO_4)_2(SiO_3)_4$ or $Ca_7R^{II}(R^{II}AlO_2)(SiO_4)_4(SiO_3)_2$.

Warwickite.—Minute slender crystals, showing characteristic copper-red reflections on the cleavage surfaces, occur in a metamorphic limestone in contact with granite at Amity, New York. Spinel and magnetite are intimately associated with the mineral, and if it be assumed that the alumina and ferric oxide found on analysis are due to these substances, and allowance be made in calculating the results, the formula $3(Mg,Fe)O, TiO_2, B_2O_3$ or $(Mg,Fe)_3TiB_2O_8$ is arrived at. This differs somewhat from the formula $6MgO, FeO, 2TiO_2, 3B_2O_3$ hitherto accepted for the species.³

Whewellite.—Large twin crystals of this rare mineral have recently been discovered associated with ankerite and barytes in a fault breccia in a coal mine near Schlan, in Bohemia. The crystals, which have been fully described,⁴ have the composition CaC_2O_4, H_2O . Allied to whewellite is an oxalate of calcium, called thierschite, investigated by Liebig in 1853. It was found as an incrustation on the marble columns of the Parthenon, and its formation appears to have been due to the action of thallophytes on the marble. An incrustation of similar origin has recently been described from limestone on the south bank of the Krym.

Wöhlerite.—Yellow prisms examined by G. P. Tschernik⁵ have a composition approximately expressed by the formula:



Xenotime.—A crystal of this mineral, resembling a cube, being a combination of the basal plane with a tetragonal prism, has been

² *J. Amer. Chem. Soc.*, 1908, **30**, 1684; *A.*, ii, 57.

³ *Amer. J. Sci.*, 1909, [iv], **27**, 179; *A.*, ii, 247.

⁴ F. Slavík, *Bull. Intern. Acad. Sci. Bohême*, 1908, **13**; *A.*, ii, 154.

⁵ *Bull. Acad. Sci. St. Pétersbourg*, 1909, 903; *A.*, ii, 1028.

found with good crystals of phenacite in pegmatite at San Miguel de Piracicaba, in Minas Geraes.⁶ The composition is as follows:

P ₂ O ₅ .	Y ₂ O ₃ , &c.	Al ₂ O ₃ +Gl ₂ O ₃ .	SiO ₂ .	Total.
33.21	62.62	3.05	1.41	100.29

Zeolite Group.—S. J. Thugutt⁷ believes that the amount of water held by zeolites depends on the size of their particles as well as on the pressure of aqueous vapour in the surrounding atmosphere, and on the period of time the material remains in contact with that atmosphere. He finds that zeolites in a fine state of division give off more water on ignition than if they have only been coarsely powdered. Apophyllite, on the other hand, loses water when ground. The composition of good crystals of *natrolite*, from Leitmeritz, with which some of his experiments were made, is represented by the formula $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}, 2\text{H}_2\text{O}$. The state of hydration of a number of zeolites has also been examined by E. Löwenstein,⁸ using van Bemmelen's method. The specimens were kept at 25° over sulphuric acid of known dilution and vapour pressure, and the loss in weight and water content was determined after equilibrium had been reached. It was found that the vapour pressure of *chabazite*, *heulandite*, and *stilbite* varies continuously with the water content, the crystals remaining clear. The zeolites of Montresta, Sardinia, previously examined to some extent by Rimatori, have also been investigated by L. Pelacani⁹ and by J. Deprat.¹⁰ The former has analysed *chabazite*, the latter *stilbite*, and both have studied *heulandite* and *mesolite*. Pelacani regards mesolite as an isomorphous mixture of scolecite and natrolite. He has observed that when chabazite is slowly heated to 350° the rate at which water is given off diminishes as the temperature rises, while for mesolite the reverse is true. Chabazite which has been heated to 350° will reabsorb water, rapidly and completely. On the other hand, in the case of mesolite, reabsorption is slow and partial. Chabazite which has been heated to redness will reabsorb about one-fourth of the total water emitted, mesolite treated similarly absorbs none at all. A specimen of *heulandite*, possessing the abnormal value of 47° for the prism angle 110:110, has been analysed by A. Serra.^{10a} His results lead to the formula $(\text{Ca}, \text{Mg}, \text{Na}, \text{K})\text{O}, \text{Al}_2\text{O}_3, \text{SiO}_2, 5\text{H}_2\text{O}$. Analyses of *heulandite* and of *stilbite* have also been published by B. Mauritz.¹¹ The *phillipsite*

⁶ E. Hussak, *Centr. Min.*, 1909, 268; *A.*, ii, 492.

⁷ *Centr. Min.*, 1909, 677; *A.*, ii, 1027.

⁸ *Zeitsch. anorg. Chem.*, 1909, 63, 69; *A.*, ii, 736.

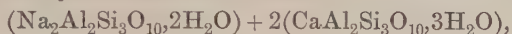
⁹ *Atti R. Accad. Lincei*, 1908, [v], 17, ii, 66; *A.*, 1908, ii, 864.

¹⁰ *Bull. Soc. franç. Min.*, 1908, 31, 181; *A.*, ii, 61.

^{10a} *Atti R. Accad. Lincei*, 1909, [v], 18, ii, 348; *A.*, 1910, ii, 48.

¹¹ *Ann. Musei. Nat. Hungarici*, 1908, 6, 537.

found in minute crystals in the basalt of Mont Simiouse, Loire,¹² can be represented as $\text{RAl}_2\text{Si}_5\text{O}_{14}, 5\text{H}_2\text{O}$ ($\text{R} = \text{Ca}, \text{K}, \text{Na}$). A detailed investigation of the zeolite, called *poonahlite*, which occurs associated with apophyllite and stilbite near Poonah, and which has usually been classed with scolecite, has shown that it crystallises in the anorthic system, has the formula:



and is identical with *mesolite*.¹³

New Minerals.

Many new minerals have been described during the past two years. Of those which exhibit well-defined physical and chemical characters, alamosite, hillebrandite, rinneite, spurrite, and villiaumite are among the most interesting. Of the rest, some, owing to lack of suitable material, have not as yet been determined with any great precision, while others owe their inclusion in our chronicle solely to the too prevalent tendency to assign new names to substances which are only varieties of well-known species. In the brief résumé which follows, the species are arranged alphabetically.

Alaite.—Hydrated vanadium oxide occurs in blood-red, mossy masses of composition $\text{V}_2\text{O}_5, \text{H}_2\text{O}$ in mines close to the Alai Mountains and South of Andijan, Siberia.¹⁴

Alamosite.—This interesting mineral is lead metasilicate, PbSiO_3 . It forms snow-white, radiating, fibrous, spheroidal aggregates, with here and there minute, colourless crystals, where single fibres have been free to develop between the spheroids. Study¹⁵ of six of these crystals proved the system to be monoclinic, $a : b : c = 1.375 : 1 : 0.924$. $\beta = 84^\circ 10'$. The crystals are elongated along the axis of symmetry, and exhibit a good cleavage perpendicular to this axis. The optic axes lie in the plane of symmetry. The crystallographic characters show analogies with those of wollastonite. The mineral was found near Alamos, Sonora, Mexico. A crystalline substance of the same composition has been obtained by S. Hilpert and P. Weiller¹⁶ in their study of the freezing-point curve of mixtures of lead oxide and silica. The artificial substance is said to crystallise in either the orthorhombic or monoclinic system, and its density, 6.36, is somewhat less than that of the mineral, 6.488.

¹² P. Barbier, *Bull. Soc. Chim.*, 1908, [iv], **3**, 822; *A.*, 1908, ii, 956; and F. Gonnard, *Bull. Soc. franç. Min.*, 1908, **31**, 269; *A.*, ii, 63.

¹³ H. L. Bowman, *Min. Mag.*, 1909, **15**, 216; *A.*, ii, 677.

¹⁴ K. A. Nenadkevitch, *Bull. Acad. Sci. St. Pétersbourg*, 1909, 185; *A.*, ii, 411.

¹⁵ C. Palache and H. E. Merwin, *Amer. J. Sci.*, 1909, [iv], **27**, 399; *A.*, ii, 676.

¹⁶ *Ber.*, 1909, **42**, 2969; *A.*, ii, 890.

Aloisiite is an amorphous hydrosilicate of a type very poor in silica. It occurs intimately mixed with calcium carbonate in the tufa of Fort Portal, Uganda.¹⁷ Its composition corresponds approximately with the formula $(R'_2R'')_4\text{SiO}_6$, where $R'=\text{Na, H}$ and $R''=\text{Fe, Ca, Mg}$.

Anophorite is a variety of alkaline hornblende found in the shonkinite rock of Katzenbuckel. It exhibits pleochroism similar to that of the mineral termed cataphorite by Brögger, from which, however, it differs in chemical composition and in optical orientation. Analysis gave the following results¹⁸:

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O
49.79	5.37	1.98	7.54	9.18	0.36	11.59	3.16	7.92	1.85	1.52

Arizonaite.—This mineral occurs in pegmatite near Hackberry, Arizona, associated with gadolinite, to which it is somewhat similar in outward appearance. Examination¹⁹ of a single, rough, imperfect crystal has led to the conclusion that the system is probably monoclinic. There is no cleavage. The density is 4.25. The mineral is dark steel-grey in colour, and opaque in the mass, but the edges of very thin fragments transmit a deep red light ($\mu > 1.84$). It is not magnetic. The mineral is completely decomposed by hot concentrated sulphuric acid, and on analysis proved to be ferric metatitanate, $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$. This compound has not hitherto been observed in Nature, but it seems probable that an iserine described by Rammelsberg,²⁰ and also a titanite iron sand from Brazil examined by J. B. Mackintosh,²¹ contain it mixed with ferrous titanate.

Bityite.—Small, yellowish-white, hexagonal prisms, with perfect basal cleavage, are found in pegmatite at Maharitra, Madagascar. Optical examination shows that the crystals are pseudo-hexagonal. $D = 3.05$. $\mu = 1.62-1.64$. The composition may be represented as follows: $10\text{SiO}_2 \cdot 8\text{Al}_2\text{O}_3 \cdot 5\frac{1}{2}(\text{Ca, Gl, Mg})\text{O} \cdot 1\frac{1}{2}(\text{Li, Na, K})_2\text{O} \cdot 7\text{H}_2\text{O}$, but as the water is only expelled at a very high temperature, the formula may be written more simply thus: $7(\text{R}'_2\text{O} + \text{R}''\text{O}) \cdot 4\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, and the mineral may be regarded as a basic orthosilicate related to staurolite and kornepine.²²

Brugnatellite.—Flesh-red laminae, resembling mica, and exhibiting good cleavage and pearly lustre, are found associated with asbestos, aragonite, magnesite, artinite, and brucite in Val

¹⁷ L. Colomba, *Atti R. Accad. Lincei*, 1908, [v], **17**, ii, 233; *A.*, 1908, ii, 956.

¹⁸ W. Freudenberg, *Mitth. d. Bad. geol. Landesanstalt*, 1908, **6**, 47.

¹⁹ C. Palmer, *Amer. J. Sci.*, 1909, [iv], **28**, 353; *A.*, ii, 1026.

²⁰ *Pogg. Ann.*, 1858, **104**, 532.

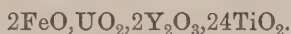
²¹ *Amer. J. Sci.*, 1885, [iii], **29**, 342.

²² A. Lacroix, *Compt. rend.*, 1908, **146**, 1367; *A.*, 1908, ii, 705.

Malenco.²³ The analytical results are satisfactorily represented by the formula $\text{MgCO}_3, 5\text{Mg}(\text{OH})_2, \text{Fe}(\text{OH})_3, 4\text{H}_2\text{O}$.

Chromitite.—The name has been given to a mineral isolated from the sand of some of the streams descending from the Kopaonik Mountains, Servia.²⁴ It occurs as minute, shining crystals, which have the formula $\text{Fe}_2\text{O}_3, \text{Cr}_2\text{O}_3$. A magnet placed at varying distances from the sand extracts from it dull crystals resembling magnetite in appearance, but which contain chromium in increasing proportion.

Delorenzite.—Black, orthorhombic crystals of a strongly radioactive mineral resembling polycrase in habit occur in the pegmatite of Craveggia, Piedmont²⁵; $a : b : c = 0.3375 : 1 : 0.3412$; $D = 4.7$. The analytical results may be expressed by the formula:



In composition the mineral is therefore closer to yttracrasite than to polycrase.

Hallerite.—This name has been suggested for a mica resembling muscovite in appearance, found at Mesvres, near Autun, and which proved on analysis to be a lithium-bearing variety of soda-mica without fluorine.²⁶

Hillebrandite.—A well-defined mineral of the formula $\text{Ca}_2\text{SiO}_4, \text{H}_2\text{O}$ has been observed²⁷ at the Terneras mine, Velardeña, Mexico, associated with yellow garnet and wollastonite, near the junction of altered limestone and intrusive basic diorite. It is fibrous in structure, but the optical characters suggest orthorhombic symmetry. The mean refractive index is about 1.61. The birefringence, weak to medium. The axial angle is medium, with strong dispersion, giving rise to abnormal blue interference tints. The mineral readily dissolves in hydrochloric acid with separation of some silica, and is slowly decomposed by water.

Hulsite.—Along the margin of the granite intrusives of the extreme western part of the Seward Peninsula, intense pneumatolytic contact metamorphism has taken place, notably in the neighbourhood of Brooks Mountain, and a considerable variety of minerals has been developed.²⁸ Among these a black, lustrous, opaque mineral is found, which somewhat resembles magnetite in appearance. It always occurs in crystals, and is associated with vesuvianite, magnetite, and brown garnet in a matrix of calcite.

²³ E. Artini, *Atti R. Accad. Lincei*, 1909, [v], 18, i, 3; *A.*, ii, 247.

²⁴ M. Z. Jovitschitsch, *Monatsh.*, 1909, 30, 39; *A.*, ii, 246.

²⁵ F. Zambonini, *Zeitsch. Kryst. Min.*, 1908, 45, 76; *A.*, 1908, ii, 604.

²⁶ P. Barbier, *Compt. rend.*, 1908, 146, 1220; *A.*, 1908, ii, 604.

²⁷ F. E. Wright, *Amer. J. Sci.*, 1908, [iv], 26, 551; *A.*, ii, 62.

²⁸ A. Knopf and W. T. Schaller, *ibid.*, 25, 323; *A.*, 1908, ii, 507.

Unfortunately the crystals do not lend themselves to exact measurement, but they probably belong to the orthorhombic system. There is a good prismatic cleavage, and the substance reacts strongly for boron. It is usually magnetic, owing to the presence of magnetite in intimate admixture. This association renders the determination of its composition difficult, but analyses of carefully selected material lead to the formula $7(\text{Fe}, \text{Mg})\text{O}, \text{Fe}_2\text{O}_3, \text{H}_2\text{O}, 4\text{B}_2\text{O}_3$.

Juddite.—This name has been given by L. L. Fermor²⁹ to a manganiferous amphibole which is found associated with blanfordite at Kácharwáhi, in the Nágpur district. The mineral, which has not as yet been fully examined, is characterised by its remarkable pleochroism.

Leesbergite.—This name was given by L. Blum³⁰ to a white, chalky mineral from the Victor iron-mine in Lorraine. It was supposed to have the formula $2\text{MgCO}_3, \text{CaCO}_3$, but W. Bruhns has shown that the composition is not constant, and regards it as a mixture with calcite or dolomite of a mineral allied to hydromagnesite, $3\text{MgCO}_3, \text{Mg}(\text{OH})_2, 3\text{H}_2\text{O}$.

Linosite.—The propriety of assigning this name to a variety of hornblende found in the island of Linosa, off the coast of Tunis, has been discussed by H. S. Washington and F. E. Wright.³¹ In view of the uncertainty of our knowledge as to the true chemical composition and relations of the hornblendes, they prefer for the present to class it with kaersutite rather than to constitute it a separate variety.

Loaisite.—A mineral discovered in Marmato by Boussingault has been assigned this name by R. L. Codazzi³² in a description of the minerals of Colombia. The published analysis agrees closely with the composition of scorodite, $\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_5, 4\text{H}_2\text{O}$, of which the substance may possibly prove to be a variety.

Natrochalcite.—This interesting and well-defined species has a composition³³ expressed by the formula



It is found in the mining district of Chuquicamata, Antofagasta, Chile, where it occurs as bright emerald-green crystals of acute pyramidal habit, belonging to the monoclinic system:

$$a : b : c = 1.423 : 1 : 1.214; \beta = 61^\circ 17\frac{1}{2}'; D = 2.33.$$

There is a good cleavage parallel to 001. The optic axes lie in the

²⁹ *Rec. geol. Surv. India*, 1908, **37**, 199; *A.*, ii, 491.

³⁰ *Mitt. geol. Landesanst. Elsass-Lothringen*, 1908, **6**, 303; *A.*, 1908, ii, 703.

³¹ *Amer. J. Sci.*, 1908, [iv], **26**, 210; *A.*, 1908, ii, 863.

³² *Centr. Min.*, 1908, 183.

³³ C. Palache and C. H. Warren, *Amer. J. Sci.*, 1908, [iv], **26**, 345; *A.*, 1908, ii, 1047.

plane of symmetry, and the acute bisectrix is inclined at 12° to the crystallographic axis c' in the acute angle β . The indices of refraction and optic axis angle for sodium light are as follows: $\alpha=1.6491$; $\beta=1.6555$; $\gamma=1.7143$. $2V=36^\circ 52'$. The axes are strongly dispersed, the angle for blue being about 3° greater than for yellow.

Ostwaldite.—It has recently been pointed out by F. Cornu³⁴ that carbon, sulphur, gold, silver, and many metallic sulphides occur in Nature as hydrogels, and he proposes to give the above name to "buttermilk silver," which he regards as the hydrogel form of silver chloride.

Paigeite is a boron mineral related to ludwigite and hulsite, and, like the latter, occurs at Brooks Mountain, Alaska.³⁵ The coal-black, lustrous, rather soft material is seen under the microscope to be composed of hair-like needles, but the system of crystallisation cannot be determined. It resembles hulsite (see p. 223) in being readily soluble in hydrochloric and hydrofluoric acids, and in reacting strongly for boron. Analyses are consistent with the formula $6(\text{Fe}, \text{Mg})\text{O}, \text{Fe}_2\text{O}_3, \text{H}_2\text{O}, 3\text{B}_2\text{O}_3$.

Paratooite.—The name has been applied to certain phosphatic materials which probably represent the remains of a deposit of bird-guano found at Elder Rock, in an arid district near Paratoo railway siding in South Australia.³⁶ Two types may be distinguished. The first occurs in yellow, encrusting masses, and is optically isotropic. The second consists of an aggregate of small, yellowish-brown, birefringent globules. The latter has a composition approximating to that of beraunite, whilst the former is essentially a hydrated phosphate of aluminium, ferric iron, and magnesium.

Plancheite.—A blue copper silicate, forming botryoidal masses or fibrous veins in limestone, is found associated with diopside at Mindouli, French Congo.³⁷ The fibres are optically biaxial and positive. The composition is $5\text{H}_2\text{O}, 15\text{CuO}, 12\text{SiO}_2$, which may be written in the form $\text{H}_2(\text{CuOH})_8\text{Cu}_7(\text{SiO}_3)_{12}$. The water is only expelled at a red heat.

Plumboniobite.—Under this name has been described a mineral resembling samarskite in composition, but containing lead.³⁸ It occurs in dark brown to black, imperfectly crystalline masses, asso-

³⁴ *Zeitsch. Chem. Ind. Kolloide*, 1909, **4**, 187; *A.*, ii, 409.

³⁵ A. Knopf and W. T. Schaller, *Amer. J. Sci.*, 1908, [iv], **25**, 330; *A.*, 1908, ii, 507.

³⁶ D. Mawson and W. T. Cooke, *Trans. Roy. Soc. South Australia*, 1907, **31**, 65; *A.*, 1908, ii, 397.

³⁷ A. Lacroix, *Compt. rend.*, 1908, **146**, 722; *A.*, 1908, ii, 508.

³⁸ O. Hauser and L. Finckh, *Ber.*, 1909, **42**, 2070; *A.*, ii, 676.

ciated with pitchblende, in the mica mines at Morogoro, Uluguru Mountains, German East Africa. Its density is 4·801 to 4·813, and the approximate percentages of its most important constituents are: C_2O_5 46, UO_2 13·7, Y_2O_3 14·5, PbO 7, FeO 6, and H_2O 6. It also contains small quantities of TiO_2 , SnO_2 , MnO , and CaO .

Rinneite.—The mineral occurs in crystalline, lenticular masses of some size, intercalated in rock salt beds, and associated with sylvine, in a mine at Nordhausen.³⁹ Analysis of pure material has shown that the substance is a triple salt of the formula $\text{FeCl}_2 \cdot 3\text{KCl} \cdot \text{NaCl}$, the whole of the iron being present in the ferrous state. A small part of the chlorine is replaced by bromine. The salt slowly oxidises in air, and cannot be recrystallised from water, but from a study of the solubility data of the salt and its components, the conditions for its artificial formation have been ascertained. The well-marked cleavage in three directions at 60° in the same zone, and the definite uniaxial interference figure suggest that it belongs to the hexagonal system, a conclusion verified by the examination of measurable crystals from Hildesheim, which have been described by O. Schneider,⁴⁰ and their isomorphism with salts of the type K_4CdCl_6 fully established.

Risörite.—The substance described in 1907 as a new yttrium columbium mineral from Risör, in Norway,⁴¹ has been the subject of further examination, and shown to be a definite species.⁴² New analyses confirm those previously given. The mineral is isotropic, exhibits considerable β -radioactivity, and may be regarded as an isomorphous mixture of fergusonite with metatitanates.

Rizopatronite.—A name used for the vanadium sulphide found at Minasragra, Peru.⁴³ It is to be regarded as a synonym of patronite, the mineral being called after Antenor Rizo-Patrona, the discoverer of the ore (compare *Ann. Report*, 1907, 302).

Rosasite.—Compact, light green, mammillated masses occur sparingly at the mines of Rosas, in Sardinia,⁴⁴ associated with malachite and aurichalcite. The composition is approximately represented by the formula $2\text{CuO} \cdot 3\text{CuCO}_3 \cdot 5\text{ZnCO}_3$.

Spurrite.—The interest of this mineral centres chiefly in its remarkable composition, $2\text{Ca}_2\text{SiO}_4 \cdot \text{CaCO}_3$. No crystals have been observed, but the optical characters, twinning, cleavage, and etched

³⁹ H. E. Boeke, *Jahrb. Min.*, 1909, 2, 19; also *Centr. Min.*, 1909, 72, and *Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 24, 632; *A.*, ii, 153 and 582.

⁴⁰ *Centr. Min.*, 1909, 503.

⁴¹ *Ann. Report*, 1907, 288.

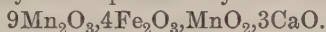
⁴² O. Hauser, *Zeitsch. anorg. Chem.*, 1908, 60, 230; *A.*, ii, 60.

⁴³ J. J. Bravo, *Chem. Zentr.*, 1908, i, 1793; from *Oesterr. Zeitsch. Berg-Hüttenwesen*, 1908, 56, 166; *A.*, 1908, ii, 703.

⁴⁴ D. Lovisato, *Atti R. Accad. Lincei*, 1908, [v], 17, ii, 723; *A.*, ii, 246.

figures indicate monoclinic symmetry.⁴⁵ The index of refraction β is approximately 1.674, and the birefringence is high. The mineral effervesces in dilute hydrochloric acid, and dissolves readily with separation of gelatinous silica. It occurs in granular masses near the junction of altered limestone and intrusive basic diorite in the Velardeña district, Mexico (compare hillebrandite, p. 223). Attempts to prepare this substance synthetically have not as yet been successful.

Sitaparite.—A dark bronze-grey mineral is found at Sitapár, in the Chhindwára district, India, which at first sight closely resembles vredenburgite (see p. 228), but is distinguished from it by its feeble magnetic properties, vredenburgite being strongly magnetic.⁴⁶ The composition may be expressed by the formula



Stellerite.—A new zeolite of the formula $\text{CaAl}_2\text{Si}_7\text{O}_{18}, 7\text{H}_2\text{O}$ has been found in one of the Aleutian Islands.⁴⁷ It crystallises in the ortho-rhombic system.

Taramellite.—This mineral is found in the granular limestone of Candoglia (Val Toce).⁴⁸ It occurs in radiating aggregates or in thin, irregular veins penetrating magnetite or pyrites. It exhibits one good cleavage, is brownish-red in colour, has a high refractive index (>1.74), and is biaxial. It is exceedingly pleochroic. The system of crystallisation is not quite certain, but is probably ortho-rhombic. The results of an analysis made on a small quantity of material agree fairly well with the formula $\text{Ba}_4\text{Fe}''\text{Fe}'''\text{Si}_{10}\text{O}_{31}$, and the mineral may be regarded as a basic salt of a polymeride of metasilicic acid, $\text{Ba}_4\text{Fe}''(\text{Fe}'''\text{O})\text{Fe}_3(\text{SiO}_3)_{10}$.

Tawmawite.—This name has been given to a dark green mineral found in fragments in the jadeite quarry at Tawmaw, Upper Burma.⁴⁹ The optical characters and composition indicate that it is a chromiferous epidote:

SiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	CaO	H_2O	Total.
37.92	12.83	11.16	9.93	25.35	2.38	99.57

Turanite is a copper vanadate, $5\text{CuO}, \text{V}_2\text{O}_5, 2\text{H}_2\text{O}$, found in spongy masses or in radio-spheroidal aggregates in mines situate near the Alai Mountains, Siberia.⁵⁰

Uhligite.—This mineral resembles perovskite in appearance, and was at first mistaken for it.⁵¹ It occurs in black, glistening

⁴⁵ F. E. Wright, *Amer. J. Sci.*, 1908, [iv], 26, 547; *A.*, ii, 62.

⁴⁶ L. L. Fermor, *Rec. geol. Surv. India*, 1908, 37, 207; *A.*, ii, 491.

⁴⁷ J. A. Morozewicz, *Bull. Acad. Sci. Cracow*, 1909, 344; *A.*, ii, 1028.

⁴⁸ E. Taccani, *Atti R. Accad. Lincei*, 1908, [v], 17, i, 810; *A.*, 1908, ii, 803.

⁴⁹ A. W. G. Bleek, *Rec. geol. Surv. India*, 1908, 36, 254; *A.*, ii, 412.

⁵⁰ K. A. Nenadkevitch, *Bull. Acad. Sci. St. Pétersbourg*, 1909, 185; *A.*, ii, 411.

⁵¹ O. Hauser, *Zeitsch. anorg. Chem.*, 1909, 63, 340; *A.*, ii, 901.

octahedra in a nepheline rock from East Africa. Analysis shows that it is an aluminous zirkelite, in which titanium predominates over zirconium, the formula being $\text{Ca}(\text{Zr},\text{Ti})\text{O}_5\cdot\text{Al}(\text{Ti},\text{Al})\text{O}_5$.

Vashegyite forms compact, dull, white masses, and is found in some abundance at the iron mine of Vashegy, Hungary.⁵² Its formula is $4\text{Al}_2\text{O}_3, 3\text{P}_2\text{O}_5, 30\text{H}_2\text{O}$. It is associated with diadochite (a sulphatophosphate of iron) and with another substance of the formula $3\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3), 2\text{P}_2\text{O}_5, 17\text{H}_2\text{O}$.

Villiaumite.—This name has been given to sodium fluoride occurring as a primary constituent of the nepheline syenite of the Island of Ruma, Los Islands, off the west coast of Africa.⁵³ It is specially characterised by its crimson colour, strong pleochroism, very low refractive index ($n=1\cdot327$), and weak birefringence. It crystallises in the tetragonal system, but is pseudo-cubic, with three perfect cleavages at right angles. It is distributed in spots through the rock, from which water extracts some 0·35 per cent. of soluble salts, consisting in the main of sodium fluoride. The mineral contains traces of potassium, calcium, and possibly of zirconium. Manganese, to which it was thought the colour might be due, could not be detected.

Vorobyevite is a variety of beryl containing caesium. It has been described by W. I. Vernadsky,⁵⁴ who concludes from a study of the best analyses that the beryls as a class have the composition $x\text{GAlAl}_2\text{Si}_4\text{O}_{12}\cdot y\text{A}$, where A is $\text{G}\text{H}_2\text{SiO}_4$, GSiO_3 (?), Cs_2SiO_3 , Li_2SiO_3 , or Na_2SiO_3 .

Vredenburgite is perhaps the most interesting of several new minerals recently described by L. L. Fermor,⁵⁵ from the manganese deposits of India. It is dull steel-grey in colour, with metallic lustre. The well-marked octahedral cleavages suggest either cubic or tetragonal symmetry. A striking property is its strong magnetism, often polar in character, and equal to that of magnetite. The simplest formula is $3\text{Mn}_3\text{O}_4, 2\text{Fe}_2\text{O}_3$, but if the iron is present as Fe_3O_4 , two analyses give the formulæ $2\text{Mn}_2\text{O}_3, 3(\text{Mn},\text{Fe})_3\text{O}_4$ and $7\text{Mn}_2\text{O}_3, 8(\text{Mn},\text{Fe})_3\text{O}_4$ respectively.

In addition to the above new minerals, two other species, as yet unnamed, may claim our attention. The first⁵⁶ of these is a phosphate of iron, possibly derived from vivianite, which has been found with trona, thenardite, and gypsum in clay about 300 kilometres north-east of Lake Tchad. The composition of this

⁵² K. Zimányi, *Zeitsch. Kryst. Min.*, 1909, **47**, 53; *A.*, ii, 900.

⁵³ A. Lacroix, *Compt. rend.*, 1908, **146**, 213; *A.*, 1908, ii, 200.

⁵⁴ *Bull. Acad. Sci. St. Pétersbourg*, 1908, 975; *A.*, 1908, ii, 955.

⁵⁵ *Rec. geol. Surv. India*, 1908, **37**, 199; *A.*, ii, 491.

⁵⁶ G. Garde, *Compt. rend.*, 1909, **148**, 1616; *A.*, ii, 676.

phosphate does not agree exactly with that of any known mineral, and is as follows:

P_2O_5 .	Fe_2O_3 .	Al_2O_3 .	CaO .	H_2O .	Resid.	Total.
33·30	44·20	1·50	2·28	20·47	0·75	99·5

The second ⁵⁷ is a nickel mineral, believed to be new, from sand ejected from Vesuvius during the eruption of April, 1906.

Meteorites.

The constituents of a number of meteorites have been analysed during the past two years, and some work of more general interest has also appeared. In the first place, we may notice that L. Fletcher⁵⁸ has shown that a compound of iron and nickel of the formula Fe_5Ni_3 possibly exists in meteorites. He was led to this conclusion by finding that when the nickel-iron of Zomba was repeatedly extracted with a solution of mercuric ammonium chloride, a gradual enrichment of the residue in nickel was brought about; a result which may be explained by the existence of a compound Fe_5Ni_3 , containing 38·5 per cent. of nickel. A similar substance seems to occur in the iron meteorites of Youndegin and Sacramento. W. Tassin⁵⁹ has made the curious observation that the Allegan meteorite contains oldhamite, CaS , apparently distributed through its ground mass in a very finely divided state. This constituent cannot be detected with the microscope, but certain portions of the stone evolve hydrogen sulphide freely when treated with an acid, and the powder, after removal of magnetic particles, was found to contain 16·66 per cent. of calcium sulphide. The same author has also investigated the composition of the chromite frequently contained in meteorites.⁶⁰ Analyses of specimens isolated from various meteorites has shown that the typical chromite composition is exceptional, but that all conform to the type RO, R_2O_3 with variable amounts of aluminium and magnesium. The structure of meteoric iron has been discussed at some length by Fraenkel and Tammann.⁶¹ They point out that a typical specimen of such an iron consists of kamacite, taenite, and a mixture of these known as plessite. When meteoric iron is heated without access of air, the kamacite first changes into granular crystals, and then the taenite begins to disappear. This change takes place even at temperatures so low as 420° , but proceeds rapidly at high temperatures. On comparing the magnetic properties of nickel-iron

⁵⁷ Casoria, *Ann. R. Scuola Super. Agric. Portici*, 1907, **7**; *A.*, ii, 155.

⁵⁸ *Min. Mag.*, 1908, **15**, 147; *A.*, ii, 65.

⁵⁹ *Proc. U.S. National Museum*, 1908, **34**, 433; *A.*, 1908, ii, 956.

⁶⁰ *Ibid.*, 685.

⁶¹ *Zeitsch. anorg. Chem.*, 1908, **60**, 416; *A.*, ii, 157.

alloys with those of meteoric iron, it was found that both lose their magnetic properties at about the same temperature, but the variation in individual pieces of meteoric iron is too great for any very accurate comparison to be made. Attempts to prepare an artificial meteoric iron led to no definite result.

Among individual meteorites we may notice the following.

Tektites.—Fragments of a substance called *moldavite*, closely resembling green bottle glass in appearance, have been found at various localities in Bohemia. They possess a peculiar external structure, and their nature and origin have given rise to much speculation. The view that they are artificial has been widely held, but in the last few years a theory propounded by F. E. Suess has made some headway. According to Suess, moldavite and substances of a somewhat similar nature found in Australia are to be regarded as meteorites of a peculiar kind, the so-called tektites. Of late this question has again been hotly debated. A study of two specimens recently found at Kuttenberg has led Weinschenk⁶² to declare himself an adherent of the meteoric theory. On the other hand, A. Rzehak⁶³ believes that these specimens are artificial, a view in which he is supported by Suess.⁶⁴ The latter, however, still holds to the meteoric theory of the origin of moldavite, and finds strong confirmation of its truth in the properties of a meteorite of glassy nature recently described by Eichstädt.⁶⁵

Ainsworth.—A coarse octahedrite found in the winter 1906-7 near Ainsworth, in Brown County, Nebraska.⁶⁶

Cañon Diablo.—Specimens consisting of a nucleus of iron surrounded by iron shale have been described.⁶⁷ The nucleus consists of schreibersite, cohenite, kamacite, taenite, and olivine, of which all except the kamacite have been analysed.

Cold Bokkeveld.—The fractured surface of a specimen of this meteorite, kept since 1865 in the Indian Museum at Calcutta, has become covered with a growth of crystals of alunogen.⁶⁸

St. Christophe-la-Chartreuse.—This stone fell in 1841, and has recently been the subject of detailed study by A. Lacroix.⁶⁹ It is a grey chondrite, consisting chiefly of olivine and hypersthene. It also contains considerable quantities of nickel-iron, felspar, and

⁶² *Centr. Min.*, 1908, 737; 1909, 545.

⁶³ *Ibid.*, 1909, 452.

⁶⁴ *Ibid.*, 1909, 462.

⁶⁵ *Geol. Fören. Förhandl.*, 1908, 30, heft 5.

⁶⁶ E. E. Howell and W. Tassin, *Amer. J. Sci.*, 1908, [iv], 25, 105; *A.*, 1908, ii, 204.

⁶⁷ G. P. Merrill and W. Tassin, *Smithsonian Miscell. Collections*, 1907, 50, 203; *A.*, ii, 591.

⁶⁸ M. Stuart, *Rec. geol. Surv. India*, 1908, 37, 2, 224.

⁶⁹ *Bull. Soc. Sci. Nat. de l'Ouest, France*, 1906, [ii], 6, 81; *A.*, ii, 248.

troilite, and smaller amounts of diopside and chromite. A monoclinic pyroxene similar to rhombic pyroxene in composition is also present. This substance, which is referred to as clinohypersthene, appears to have crystallised out from the fused rhombic pyroxene, and is identical with the magnesia-pyroxene prepared artificially.

Schafstädt.—This stone was supposed by C. Klein to be the unique representative of a group of meteorites containing leucite; there seems, however, to be good reason for believing that it is merely a piece of leucite-basanite lava from Vesuvius.⁷⁰

Williamstown.—This meteorite is a typical octahedrite of medium coarseness.⁷¹ Kamacite, taenite, and plessite are present, with here and there nodules of troilite, some of which enclose carbonaceous matter, and are usually bounded by a thin line of schreibersite.

In conclusion, attention must be called to the recent issue of a second Appendix to the sixth edition of Dana's "System of Mineralogy," making this invaluable work complete up to the beginning of the year 1909.

A. HUTCHINSON.

⁷⁰ M. Belowsky, *Centr. Min.*, 1909, 289; *A.*, ii, 592.

⁷¹ E. E. Howell and W. Tassin, *Amer. J. Sci.*, 1908, [iv], 25, 49; *A.*, 1908, ii, 203

RADIOACTIVITY.¹

α -Rays.

IN previous Reports the evidence has been given for the conclusion that the α -radiation from radioactive substances is due to the expulsion of positively charged particles of atomic dimensions with a velocity of the order of about one-fifteenth that of light. The initial velocity of expulsion is the same for all the α -particles of any one type of radioactive matter, but differs, within somewhat narrow limits, for the different types. The mass, however, is identical in all cases, and is $2n$ times that of hydrogen, where n is the number of atomic charges carried by the α -particle, which may be compared with the valency of an ion in electrolysis. Methods have now been developed which have enabled the number of α -particles expelled from a radioactive substance to be directly counted, and these have established that $n=2$. The atomic weight, therefore, of the α -particle is 4. Other evidence has proved directly the identity of the α -particle with the helium atom, a result long indirectly foreshadowed. The theory of probability applied to radioactive changes² leads to the conclusion that, when the numbers of atoms disintegrating in unit time is few, variations from the average number may be anticipated, inversely proportional in magnitude to the square root of that number. Such rapid variations in the intensity of α -radiation, and therefore of the ionisation, from a constant source, in part observed unwittingly,³ in part sought for deliberately⁴ make themselves apparent, especially when the ionisation currents of two separate similar preparations are balanced against each other. Complete balance is never so attained, the indicating instrument showing perpetual excursions on either side of the zero position. This phenomenon has now been thoroughly studied,⁵ and found to be due to real variations in the rate of

¹ This report covers the years 1908 and 1909.

² E. von Schweidler, *Beibl. Ann. Physik.*, 1907, **31**, 356.

³ H. L. Bronson, *Phil. Mag.*, 1906, [vi], **11**, 143.

⁴ K. W. F. Kohlrausch, *Sitzungsber. K. Akad. Wiss. Wien*, 1906, **115**, (iia), 673.

⁵ E. Meyer and E. Regener, *Ann. Physik*, 1903, [iv], **25**, 757; H. Geiger, *Phil. Mag.*, 1908, [vi], **15**, 539.

expulsion of α -particles, which have been shown, although the result has been subject to some criticism,⁶ to follow the law deduced from the theory of probability.

Two independent methods have been now developed which are sufficiently sensitive to enable the effect of a single α -particle to be recorded. The first⁷ makes use of the scintillations produced in zinc sulphide, the discontinuity of which in the spinthariscopes has long been known. A definite small portion of the zinc sulphide screen, faintly illuminated to assist in focussing, is viewed through a microscope of suitable aperture and magnification, so that the picture appears in not less than its natural brightness. Under these conditions, for which the original paper may be profitably consulted, the number of scintillations in the field of vision can readily be counted, when the intensity of the source is such that they do not exceed more than one every few seconds. In the second method,⁸ which is less simple, but offers more guarantee that all the α -particles expelled are counted, the ionisation in the gas produced by the α -particle is magnified by the application of a potential at the electrodes so great that the gas is near the breaking-down point at which a disruptive discharge would pass. In these circumstances the ions produced themselves become ionising agencies—the negative ions more readily than the positive—by virtue of the kinetic energy acquired under the field, and produce fresh ions in their path by collisions. The field is adjusted so that only the negative ions so ionise, and the magnification of the effect is then large but not infinite, the energy of the α -particles, as it were, merely pulling the trigger whereby a much larger quantity of the energy of the electric field is released. Fields of the order of 1000 volts per cm., and a gas pressure of about 5 cm., were employed. The α -rays from a powerful source traverse an exhausted tube several metres in length, and pass through a minute aperture along the axis of the detecting chamber, which consists of a narrow cylinder, connected to the high voltage battery, carrying a central electrode connected with the electrometer. The arrival of each α -particle causes the electrometer needle to move with a sudden jerk, after which, by means of a suitable “air resistance,” it automatically returns again to zero. The number of jerks—usually adjusted to one every few seconds—gives the number of α -particles entering the detecting chamber. From geometrical considerations, the total number expelled from the source can thus be deduced.

⁶ N. Campbell, *Proc. Camb. Phil. Soc.*, 1909, **15**, 117.

⁷ E. Regener, *Ber. Deut. physikal. Ges.*, 1908, 78.

⁸ E. Rutherford and H. Geiger, *Proc. Roy. Soc.*, 1908, **81**, A, 141; *A.*, 1908, ii, 555.

In this way, it was found that 3.4×10^{10} α -particles are expelled per second from the radium-*C* in equilibrium with 1 gram of radium. This fundamental constant will be termed *Q*. Each of the first four α -ray changes of radium give the same number of α -particles.⁹ Hence this number holds equally for radium itself, the emanation, and radium-*A*, the total number per second from 1 gram of radium in equilibrium¹⁰ being therefore 1.36×10^{10} per second. Taking the limit of detection of minute quantities of radium by the emanation test as 10^{-12} gram,¹¹ it follows that this corresponds with the expulsion of only one α -particle every 100 seconds, and, indeed, the von Schweidler variation is easily detectable by the irregular motion of the gold-leaf in such measurements.

A comparison of the results of the electric and scintillation methods showed that both gave the same result, so that under suitable conditions each α -particle produces a scintillation. This being the case, it is probable that the scintillation method, on account of its simplicity, will be widely employed, and will supplant the electric method almost completely.

The electric and fluorescence methods have, since the above account was written, been supplemented by a third, depending on the photographic action of the α -rays. It has been shown that each halide grain in the film struck by an α -particle is rendered capable of development, and the method appears to consist in counting the number of opaque grains in the film by means of a microscope. It is claimed that it is applicable to very weak sources by the use of very long exposures, and to α -particles of very short range.¹²

From the total positive charge carried by the α -particles from a known mass of radium, the individual charge on each α -particle was deduced to be 9.3×10^{-10} E.S.U.¹³ This is between two and three times the previously accepted value of the single atomic charge, 3.4×10^{-10} , but there is now good reason for believing that the older determinations, by the well-known cloud method, gave too low a value, and that 4.65×10^{-10} , or one-half of the charge on the α -particle, is nearer the truth. More recent determinations by the cloud method¹⁴ have given 4.65, whilst the study of the Brownian movement in liquids¹⁵ has given 4.1. By the aid of the ultra-microscope, the same constant has also been determined for the

⁹ *Ann. Report*, 1905, 296.

¹⁰ Compare *ibid.*, 295 (line 8 from bottom).

¹¹ F. Soddy, *Phil. Mag.*, 1909, [vi], 18, 851; *A.*, 1910, ii, 10.

¹² S. Kineshita, Royal Soc. Meeting, 9/12/09 (abstract only available).

¹³ E. Rutherford and H. Geiger, *Proc. Roy. Soc.*, 1908, 81, A, 162; *A.*, 1908, ii, 794.

¹⁴ Millikan and Begeman, *Physical Rev.*, 1908, 197; R. A. Millikan, *Phil. Mag.*, 1910, [vi], 19, 209.

¹⁵ J. Perrin, *Ann. Chim. Phys.*, 1909, [viii], 18, 1.

charged fine dust produced in a gas by the arc between metallic electrodes,¹⁶ and found to be 4.6. From Planck's theory of radiation, the value 4.69 has been found. There is thus a considerable body of evidence¹⁷ that the α -particle carries two atomic charges, and the value of its atomic mass is therefore 4. Dividing the farad by the new value of the atomic charge leads to the result that there are 6.2×10^{23} atoms in one gram of hydrogen. The period of average life of radium, since the atomic weight is known, can be deduced from the number of atoms in one gram and the number of α -particles expelled per second, on the assumption that *only one α -particle* is expelled per atom disintegrating. The value so found (2560 years) agrees so well with the best determinations that it may now be considered definitely proved that only one α -particle is so expelled. The theoretical volume of emanation in equilibrium with one gram of radium, on the assumption that one molecule of mon-atomic emanation results from one atom of radium disintegrating, is 0.585 cu. mm. at N.T.P., whereas the theoretical rate of production of helium, four atoms of helium resulting from each atom of radium disintegrating, is 158 cu. mm. per year. The theoretical heating effect of the α -particles from one gram of radium is 113 gram cal. per hour. These fundamental quantities, calculated from the value of Q , are all so completely borne out by experiment, that no doubt remains of the essential accuracy of the underlying assumptions.

The identity of the α -particle with helium has also been proved in the most complete manner.¹⁸ The emanation from 140 milligrams of radium was stored in exceedingly thin-walled glass tubes surrounded by an outer exhausted jacket. The tubes were proved to be perfectly gas-tight and impervious to the passage of ordinary gaseous helium, but their thickness was less than the range of the α -particle in glass, so that practically all the α -particles expelled from the enclosed emanation penetrated, with diminished velocity, the glass walls of the tube. The presence of helium in the outer surrounding jacket was tested for by filling it with mercury and compressing its contents into a tiny spectrum tube. In this way the passage of helium in the form of α -particles through the gas-tight glass tube was decisively shown. As is to be expected, the α -particles, owing to their velocity of projection, bury themselves to a slight depth in the wall of the outer jacket, and an appreciable time is taken for the helium to diffuse out. By wrapping lead foil round similar thin tubes, filled with emanation, and not surrounded by a jacket but left exposed to the air, and subsequently melting the

¹⁶ F. Ehrenhaft, *Physikal. Zeitsch.*, 1909, **10**, 308.

¹⁷ Compare also M. Moulin, *Le Radium*, 1909, **6**, 164.

¹⁸ E. Rutherford and T. Royds, *Phil. Mag.*, 1909, [vi], **17**, 281; *A.*, ii, 203.

lead in a charcoal vacuum, it was proved that the lead retains some of the helium it receives during its bombardment with α -particles. The same lead not so treated gave no helium when melted. This removes the last possible objection that the helium was in the glass all the time and merely liberated by the action of the α -particles.

In view of the simplicity and directness of the radium series of changes, each successive α -ray disintegration giving one atom of helium from each atom undergoing disintegration, it might be concluded that other α -ray changes would be similar. It is, however, in the highest degree significant that this does not appear to be the case. The relative ionisation given by the emanation and the active deposit of thorium and actinium respectively¹⁹ is in each case such as would result if twice as many α -particles were given off in the change of the emanation as in the change of the active deposit. As there is conclusive indirect evidence²⁰ that in the change of the thorium active deposit two α -particles of different range are emitted, probably in consecutive changes so rapid that they still defy analysis, it appears that four α -particles at least must result from one atom of thorium emanation on disintegration. So far, the α -rays of the active deposit of actinium have been considered homogeneous, and due to actinium-*B*, but anomalies in the α -ray range curves have now been observed²¹ for this case also, and a similar explanation to that for the thorium active deposit has been suggested. Here, however, the difference in the ranges can only amount to a few millimetres of air, and the matter is not so definite. If the explanation is correct, the actinium emanation must also give at least four α -particles. The case of uranium, which appears to give two α -particles, will be again referred to. The number of ions (presumably pairs of ions are referred to) produced by the α -particle of radium-*C* during its whole range in air has been redetermined²² on the new data to be 2.37×10^5 . The specific ionisation at each point of the range has been determined. At the end of the range this diminishes very rapidly, but still not absolutely abruptly. The data obtained allows the number in the case of any other α -particle of different range to be calculated. The estimation of small quantities of radium by means of the saturation ionisation current in air at low pressure, using a small part only of the range of the α -particles, is suggested.

The scattering of the α -particles in passage through air and

¹⁹ H. L. Bronson, *Phil. Mag.*, 1908, [vi], 16, 291; *A.*, 1908, ii, 792.

²⁰ *Ann. Report*, 1906, 342.

²¹ Mlle. L. Blanquies, *Compt. rend.*, 1909, 148, 1753; *Le Radium*, 1909, 6, 230; *A.*, ii, 634.

²² H. Geiger, *Proc. Roy. Soc.*, 1909, 82, A, 358.

metals²³ has been re-examined by the scintillation method.²⁴ In a good vacuum there is no scattering, but a single gold leaf is sufficient to cause notable scattering of the beam. It has also been established²⁵ that a diffuse reflection of α -rays occurs from the incident surface of a metal struck by α -rays, which is the greater the greater the atomic weight of the metal. Gold returns about twenty times as many α -particles as aluminium. In one experiment with platinum, about 1 in 8000 of the α -particles was reflected. The effect attains a maximum very quickly when the thickness of the reflector is increased, about half the maximum being attained by a thickness equivalent to only 2 mm. of air. Further search for any indication of the α -particle after it has passed its critical distance at which ionisation ceases²⁶ has resulted in failure. It has been shown that the positive charge transported by the particles and the secondary emission of electrons produced on impact cannot be detected beyond the critical distance.²⁷ It appears certain that the α -particle is quite suddenly stopped at the end of its detectable path, and becomes an ordinary atom of helium, but its kinetic energy at this point is still considerable, and may possibly furnish a source necessary for any process of atomic synthesis.²⁸

It is known that the heavier metals absorb the α -rays more strongly at the end of their path than initially.²⁹ The "air equivalent" of the metal, or thickness of air equivalent to a given thickness of metal, increases as the range increases. Paper and similar substances have air equivalents independent of the range, but in hydrogen the "hydrogen equivalent" increases for these substances as with the metals. The effects are cases of a general law that if the stopping power of any substance is taken as the standard, the relative stopping powers of substances of greater atomic weight than the standard increase as the range of the α -particle increases, while for substances of less atomic weight than the standard the converse is true.³⁰

The phenomenon of "initial recombination"³¹ shown exclusively by the ionisation produced by α -rays has received an elegant

²³ *Ann. Report*, 1906, 335.

²⁴ H. Geiger, *Proc. Roy. Soc.*, 1908, **81**, A, 174; *A.*, 1908, ii, 795.

²⁵ H. Geiger and E. Marsden, *Proc. Roy. Soc.*, 1909, **82**, A, 495; *A.*, ii, 782.

²⁶ *Ann. Report*, 1906, 335.

²⁷ E. Aschkinass, *Ann. Physik*, 1908, [iv], **27**, 377; *A.*, 1908, ii, 920; W. Duane, *Amer. J. Sci.*, 1908, [iv], **26**, 464; *Compt. rend.*, 1908, **146**, 958 and 1089; *A.*, 1908, ii, 553, 554.

²⁸ Compare W. H. Bragg, *Presidential Address: Australian Assoc.*, 1909.

²⁹ *Ann. Report*, 1907, 312.

³⁰ T. S. Taylor, *Amer. J. Sci.*, 1908, [iv], **26**, 169; *A.*, 1908, ii, 783; *Phil. Mag.*, 1909, [vi], **18**, 604; *A.*, ii, 850; *Physical Rev.*, 1909, **28**, 465.

³¹ *Ann. Report*, 1906, 338.

explanation. The α -particle leaves behind in its flight a long column of ions of cross section corresponding with that of the α -particle. Thus, in air at atmospheric pressure, the passage of an α -particle will leave about 10^5 pairs of ions crowded into 3 cm. length of one of these narrow columns. The real concentration of the ions in these columns is far greater than the average concentration for the whole gas, and recombination is favoured. Even a very intense electric field acting normally to the trajectories of the rays cannot completely prevent recombination, whereas it has been found that if the field acts at right angles to the trajectories the saturation current is far more readily and completely obtained.³² This seems to render unnecessary the earlier view that the ions generated from one atom were caught and prevented from escaping by other atoms in the same molecule.

β -Rays.

As is well known, the ratio e/m of the charge to the mass of the β -particle diminishes rapidly as the velocity (v) of the particle approaches that of light, and this has been generally explained by the increase in the (purely electromagnetic) mass of the electron at high velocity. The variation of e/m with v for the β -particles of radium has been redetermined³³ with great accuracy, and the various mathematical equations which have been proposed on theoretical grounds to express the law of variation have been thus subjected to experimental test. A grain of pure radium fluoride was placed in the centre of two parallel circular plates, 0.25 mm. apart, electrically charged to opposite sign. A photographic film on the inside of a cylinder coaxial with the plates and of twice their diameter received the trace of the deflected rays. A magnetic field acted in the direction parallel to one diameter of the plates. Thus it was ensured that only those rays escaped and reached the film for which the electrostatic deviation inside the plates exactly balanced the electromagnetic deviation. After the rays had escaped from the parallel plates, the magnetic force alone operated. If α is the angle between the direction of the rays and that of the magnetic field, and H and F are the strengths of the magnetic and electric fields respectively, $V = \frac{F}{H \sin \alpha}$, or, in words, each point on the photographic trace corresponds with rays of a definite known velocity, fixed by the conditions of the experiment. The deviation of the trace at each point from the plane of the parallel plates

³² M. Moulin, *Compt. rend.*, 1909, **148**, 1757; *Le Radium*, 1908, **5**, 136; *A.*, 1908, ii, 921. The theory is ascribed to M. Langevin.

³³ A. H. Bucherer, *Physikal. Zeitsch.*, 1908, **9**, 755.

thus gives the magnetic deflection of homogeneous rays of known velocity, and so the variation of e/m with velocity is determined. As a result, it was established that $e/m_0 = 1.705 \times 10^7$, where m_0 represents the mass at low speeds, and $e/m = e/m_0(1 - \beta^2)^{\frac{1}{2}}$, where β is the ratio of the velocity of the particle to that of light. This is the Lorentz theoretical equation, and its experimental proof appears also to have important metaphysical consequences in establishing the Lorentz-Einstein principle of relativity.

Measurements³⁴ of the amount of negative electricity transported in a high vacuum from the bare active deposit of radium have led to the conclusion that as many electrons are emitted in the change of radium-*B* as in that of radium-*C*, and that for each α -particle from the latter there must be at least 20 and probably 50 electrons emitted. The electric and magnetic deflection of these electrons shows, however, that most of them move with the relatively feeble velocity of less than 4×10^8 cm. per second. They would thus possess very little penetrating power, and must be due to rays of the δ type, rather than to true penetrating β -rays. Over the distance of 0.5 mm. in air from the bare surface, however, they produce intense ionisation, comparable with that produced by the α -particles of radium-*C*. This perhaps explains the probably erroneous statement that radium-*B* emits α -particles.³⁵

With reference to the true β -particles emitted by radium-*C*, other experiments³⁶ have indicated that probably only one, or possibly two β -particles are emitted for each α -particle. The negative charge communicated in a high vacuum to an insulated brass cylinder, connected to an electrometer, from a glass tube, of wall thickness 0.078 mm., containing radium emanation, placed inside the cylinder, corresponded with 3.7×10^{10} β -particles per second (referred to 1 gram of radium), assuming the charge on each particle to be 4.67×10^{-10} E.S.U. Corrections for a small proportion of the β -particles of radium-*C* absorbed in the glass, and also for a small proportion of those from radium-*B* able to get through, gave the number 5.0×10^{10} (for radium-*C* alone). This correction involves, however, the unproved assumption that the total number of β -particles expelled from radium-*B* is equal to that from radium-*C*, and is therefore preliminary.

³⁴ W. Duane, *Le Radium*, 1908, 5, 71; *Amer. J. Sci.*, 1908, [iv], 26, 1; *A.*, 1908, ii, 748; E. Aschkinass, *Ann. Report*, 1907, 315; *Ann. Physik*, 1908, [iv], 27, 377; *A.*, 1908, ii, 920.

³⁵ *Ann. Report*, 1906, 346 and 347; F. A. Harvey, *Physikal. Zeitsch.*, 1909, 10, 46; *A.*, ii, 203 (also *Physical Rev.*, 1909); H. L. Bronson, *Physikal. Zeitsch.*, 1909, 10, 393; *A.*, ii, 634.

³⁶ W. Makower, *Phil. Mag.*, 1909, [vi], 17, 171; *A.*, ii, 204; *Brit. Ass. Rep.*, 1908, 601.

A fundamentally important consequence of the same experiments is the proof that the *number* of β -particles penetrating successive thicknesses of matter is reduced according to the same exponential law as when the absorption is determined in the usual way by measuring the ionisation the emergent particles can produce. The whole question of the nature of the β -rays, whether homogeneous or heterogeneous as regards velocity, and the exact meaning to be attached to their "absorption" in passage through matter,³⁷ is, in spite of numerous researches, still in a highly controversial state, and would scarcely repay very detailed discussion at the present stage.

In the first place, it has been established³⁸ that in passage through matter far more of the β -rays are scattered out of their original direction than are completely stopped, and relatively very thin screens—0.01 cm. of aluminium, or 0.002 cm. of gold—completely scatter a pencil of β -rays in all directions. Scattering alone can be represented by an exponential equation with a numerical "coefficient of scattering," which is for all substances about thirteen times greater than the true coefficient of absorption. This easy scattering is one of the many difficulties which make any exact theory of the nature of the absorption of β -rays difficult to establish.

In the second place, it appears that the so-called absorption-coefficient is very much influenced by relatively small differences in velocity. Thus, comparing the β -radiations of uranium-*X* and radium-*E*₂, the absorption-coefficients in aluminium are respectively 14 and 40 (cm.)⁻¹, whereas the velocities are, according to new determinations,³⁹ 2.76×10^{10} and 2.31×10^{10} cm. per second. Recent work to be considered has shown that if single β -ray products are dealt with, the absorption tends to be in almost all cases purely exponential, and since it is known that the number of β -particles is exponentially diminished, it follows that the velocity of the emergent particles is not altered by their passage through matter, for a diminution in velocity far too small to be directly detected by magnetic deflection methods would have a large influence in increasing the absorption-coefficient. Revolutionary conclusions, it is true, as to the heterogeneity of β -rays and their linear rather than exponential absorption by matter have been recently put forward, but it remains very open to question whether the methods employed were refined enough to bear such an interpretation.⁴⁰

³⁷ For a full discussion of the alternative possibilities at issue, see *Ann. Report*, 1907, 315.

³⁸ J. A. Crowther, *Proc. Roy. Soc.*, 1903, **80**, A, 186; *A.*, 1908, ii, 247; *Proc. Camb. Phil. Soc.*, 1909, **15**, 273; J. P. V. Madsen, *Phil. Mag.*, 1909 [vi], **18**, 909; *A.*, 1910, ii, 7.

³⁹ H. W. Schmidt, *Physikal. Zeitsch.*, 1908, **9**, 6.

⁴⁰ W. Wilson, *Proc. Roy. Soc.*, 1909, **82**, A, 612; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1909, **10**, 948; *A.*, 1910, ii, 8; W. Wilson, *ibid.*, 1910, **11**, 101.

A working theory has been put forward, which, although almost certainly not rigidly true, has proved extraordinarily fruitful of new discoveries, according to which only one type of β -radiation is given out in each disintegration, and this radiation is strictly homogeneous as regards velocity and is absorbed by matter according to a purely exponential law. Departures of the β -ray absorption curves from this law indicate complexity of the β -rays, due to their being derived from more than one disintegration product.⁴¹ In order to avoid, as far as possible, complications due to "secondary" β -rays, aluminium is used as the absorbing material in taking the absorption curves, and the diameter of the electroscope is large compared with that of the pencil of rays to include also scattered radiation. In these circumstances, according to this theory, if the absorption curve of the β -rays is not exponential, a complex disintegration of more than one β -ray product is indicated, and in many cases where new β -ray products have been indicated in this way, they have subsequently been found to exist, and have been separated by new methods. It may be remarked in passing, however, that such a true exponential absorption applies at best only over a limited range. Thus, the penetrating β -radiation of uranium- X , from the first regarded as an example of homogeneous β -radiation, and for which even now no evidence of complexity has been advanced, is *not* exponentially absorbed by aluminium in any circumstances, the absorption-coefficient increasing continually and regularly to nearly three times the initial value before the rays are all absorbed.⁴² The advocates of the theory seem disposed to regard all such phenomena as due to unsuitable conditions of measurement, but it is to be noted that they have never yet shown a true exponential absorption curve except over a short range. It seems as though the β -particle probably does suffer some reduction in velocity in passage through matter, accounting for this change of the absorption-coefficient, although this diminution may well be too small to be detected directly by magnetic measurements.⁴³

It has also been found impossible completely to deviate the β -rays of either uranium or radium by magnetic fields several times as strong as is sufficient to deviate the great majority of the rays, and a very small proportion of the β -rays in each case seem to possess velocities very nearly indeed approaching that of light itself.⁴⁴ Nevertheless, it has been established for a great number of single β -ray products that pure exponential absorption of the

⁴¹ O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1908, **9**, 321; *A.*, 1908, ii, 452.

⁴² M. Levin, *ibid.*, 1907, **8**, 585; *A.*, 1907, ii, 836.

⁴³ H. W. Schmidt, *ibid.*, 1909, **10**, 929; *A.*, 1910, ii, 7.

⁴⁴ F. Soddy, *Phil. Mag.*, 1909, [vi], **18**, 858; *A.*, 1910, ii, 10.

rays can be obtained over short ranges by suitable methods of measurement, and only a few exceptions to the rule now remain to be cleared up.

In the following table, compiled from a mass of observations,⁴⁵ are collected the substances giving β -rays homogeneous in this sense, together with the thickness in mm. of aluminium necessary to cut down the β -rays to half-value.

Thorium- <i>A</i>	0.05	Radium- <i>B</i>	0.09
Thorium- <i>D</i>	0.441	Radium- <i>E</i> ₂	0.162
Uranium- <i>X</i>	{ 0.434	Radioactinium	0.04
	{ 0.012	Actinium- <i>A</i> less than	0.04
Radium.....	0.022	Actinium- <i>C</i>	0.24

A new short-lived product intermediate between meso-thorium and radio-thorium, known as thorium-2, also gives β -rays, which, however, appear complex. Radium-*C* gives probably two types of β -rays of not very different penetrating power, and a partial resolution of radium-*C* into two successive products has been effected. The list comprises many substances either new or not before suspected of giving β -rays, but in all such cases the β -radiation is of a very feeble penetrating power, which accounts for their either being wrongly ascribed to α -rays, or to their not being at first recognised as definite specific β -radiations. Whatever may be thought of the truth of the underlying conceptions, their fruitfulness in the discovery of new disintegration products cannot be denied. The further logical extension of this point of view, that each disintegration gives out one, and one only, definite homogeneous type of radiation—that when a substance gives out both α - and β -rays together, as, for example, radium itself and radium-*C*, they must be derived from successive changes—does not appear yet to be experimentally justified.

γ -Rays.

A great impetus has been given to the study of the γ -rays from the physical standpoint by the theory⁴⁶ that they also, like the β -rays, consist in the emission of discrete particles, rather than of pulses or waves of electromagnetic character similar to light. The theory, which is known as the neutral-pair theory, in that the discrete γ -particle is supposed to consist of an electrically neutral couplet composed of one negative and one, still itself unknown, positive electron, has hardly been seriously opposed so far as the γ -rays themselves are concerned. It is its further extension to the

⁴⁵ O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1908, **9**, 321, 649 and 697; *A.*, 1908, ii, 452, 920, 1007; 1909, **10**, 697 and 741; *A.*, ii, 849, 954; O. Hahn, *ibid.*, 1908, **9**, 246; *A.*, 1908, ii, 484.

⁴⁶ *Ann. Report*, 1907, 321.

X-rays, and ultimately possibly even to light itself, that has aroused opposition, and it is not difficult to foresee that the growth of the theory threatens to reopen fundamental questions of the nature of electromagnetic radiations in general and to modify the old undulatory theory, so as to bring it more into harmony with the modern views as to the discrete nature of the electric charge. A full consideration of the general question would be manifestly impossible here. The γ -rays only can be considered, although, as already remarked, this is to confine the evidence mainly to the side in favour of the newer theory. It is recognised that the γ -rays, directly, produce little, if any, detectable action. Their ionisation and other effects have been traced, at least mainly, to the secondary β -rays, into which they are in part transformed in passage through matter. On the new view a certain proportion of the neutral pairs is broken up on impact with atoms, the negative partner being liberated as a detectable β -particle. The main evidence in favour of the theory is that the γ -ray possesses momentum in the direction of its propagation. The secondary β -particles they generate move at first mainly in the direction of the original beam, whereas on the older pulse theory no such asymmetry is to be anticipated. The consequence is that there exists great disproportionality in the amount of secondary β -radiation from the incident and emergent faces of a plate traversed normally by a pencil of γ -radiation. It is easy to tell from this, without otherwise knowing, in which direction the γ -ray is moving, whilst on the older pulse theory this would be impossible.⁴⁷ A tendency from this point of view is to regard the β - and γ -radiation as mutually convertible in their passage through matter. The production of secondary γ -rays from β -rays has, however, not hitherto been observed,⁴⁸ although the existence of a feeble secondary γ -radiation produced by γ -rays has now been well established.⁴⁹ The interdependence of the primary β - and γ -radiation is questioned also on account of the great relative poverty in γ -rays, as compared to β -rays, shown by uranium as contrasted with radium.⁵⁰ Experiments on intensely active preparations of uranium-X, prepared from large quantities of uranium, have shown that the γ -rays possess, contrary to prior statements, only slightly less penetrating power than those from radium,⁵¹ but

⁴⁷ W. H. Bragg and J. P. V. Madsen, *Phil. Mag.*, 1908, [vi], **15**, 663; *A.*, 1908, ii, 556; **16**, 918; *A.*, ii, 112.

⁴⁸ H. Starke, *Ber. Deut. physikal. Ges.*, 1908, **10**, 267; *A.*, 1908, ii, 341.

⁴⁹ R. D. Kleeman, *Phil. Mag.*, 1908, [vi], **15**, 639; *A.*, 1908, ii, 553; A. S. Eve, *ibid.*, **16**, 224; *A.*, 1908, ii, 795; *ibid.*, 1909, **18**, 275; *A.*, ii, 783; J. P. V. Madsen, *ibid.*, **17**, 423; *A.*, ii, 365.

⁵⁰ F. Soddy and A. S. Russell, *Phil. Mag.*, 1909, [vi], **18**, 620; *A.*, ii, 851.

⁵¹ Compare *Ann. Report*, 1906, 352.

in proportion to the β -radiation they are over sixty times less powerful. The γ -rays are shown, with suitable methods of measurements, to be exponentially absorbed by matter (after a certain initial thickness), the absorption-coefficient having been redetermined for both radium and uranium γ -rays for a number of substances and shown to be nearly proportional to the density. Certain fruitful sources of confusion in previous measurements with regard to the numerical value of these coefficients have been cleared up.

A second and perhaps more essential modification brought about by the new theory concerns the source of energy of the secondary β - or cathode-radiation produced by γ -rays and X -rays respectively, in that it is ascribed to the energy of the primary beam, rather than to the internal energy of the atoms subjected to the radiation. The effects dealt with are in general complicated, more than one type of secondary radiation being produced. In the first place, the velocity of a part of the secondary β -rays produced by γ -rays appears to approximate to the velocity of the primary β -rays.⁵² This is in favour of the view that the β - and γ -rays are mutually convertible. In the second place, there is a tendency to explain the variations of secondary radiation with the atomic weight of the radiator,⁵³ without recourse to the view that any specific secondary radiation is emitted by the atoms of the radiator.⁵⁴

An earlier view, that the primary radiation acted as the trigger to release a certain internal store of energy from the atom in the form of secondary β -radiation, travelling with a velocity dependent on the nature of the atom rather than on that of the primary beam, is on its trial. It appears rather as if the character of the primary beam, and not at all that of the atom, decided the nature of the secondary radiation.

Thermo-Radioactivity.

The heat evolution of more than 1 gram of radium chloride, containing 0.7951 gram of radium (element) as determined by atomic weight estimations, has been redetermined. The conditions were somewhat indefinite as regards the proportion of the energy of the *penetrating* radiations converted into heat, the rays having to penetrate 1 mm. of glass and 5 mm. of copper before escaping from the calorimeter, so that all the β -radiation and a small part of the γ -radiation would be absorbed. The result was that 1 gram of

⁵² R. D. Kleeman, *Proc. Roy. Soc.*, 1909, **82**, A, 128; *A.*, ii, 364.

⁵³ *Ann. Report*, 1906, 350; 1907, 318.

⁵⁴ W. H. Bragg and J. P. V. Madsen, *Phil. Mag.*, 1908, [vi], **16**, 692; *A.*, 1908, ii, 921; J. P. V. Madsen, *ibid.*, 1909, **18**, 909; *A.*, 1910, ii, 7.

radium (element), in equilibrium with its products as far as radium-*C*, generates 118.0 gram-calories per hour. The uncertainty attaching to the amount of the products radium-*D* to radium-*F* in the preparation was not greater than 1/2 per cent.⁵⁵

A real advance in the measurement of minute evolutions of heat from radioactive preparations appears to have been made in the construction of a calorimeter capable of measuring the evolution of 0.001 gram-calorie per hour.⁵⁶ The apparatus consisted of two similar exhausted vessels, half full of ether, connected from below the ether-level by a capillary gauge containing a gas bubble, the motion of which was observed. The evolution of heat is recorded by the rise in the vapour pressure of the ether surrounding the preparation. The whole was elaborately insulated from external thermal influences, and the preparation to be tested was placed inside one of the vessels, together with a Peltier couple of iron-nickel, which was cooled by the passage of a current to neutralise exactly the heat evolved from the radioactive preparation. A preliminary determination with 0.8 milligram of radium chloride gave 120 calories per gram of radium per hour. A radio-thorium preparation gave 0.025 cal. per hour, which was of the same order as that from radium of similar activity. A polonium preparation gave 0.0117 cal. per hour. In the latter case, it was calculated that a quantity of radium giving the same ionisation current as the polonium would have given 0.011, so the result is favourable to the view that the heat disengaged is almost entirely due to the kinetic energy of the α -particles expelled.

A determination of the heat generated by thorium oxide has given as the result that 1 gram, in equilibrium with its products of disintegration, gives 2.1×10^{-5} calories per hour, which is 3.2×10^6 times less than that given by radium in equilibrium.⁵⁷ Experiments have also been made on pitchblende, but final results are not yet to hand.⁵⁸ The earlier observation that the absorption of X-rays in lead produces more heat than in zinc has now been definitely shown to be erroneous.⁵⁹

⁵⁵ E. v. Schweidler and V. F. Hess, *Sitzungsber. K. Akad. Wiss. Wien*, 1908, **117**, (iia), 879.

⁵⁶ W. Duane, *Compt. rend.*, 1909, **148**, 1448 and 1665; *A.*, ii, 534, 637.

⁵⁷ G. B. Pegram and H. W. Webb, *Physical Rev.*, 1908, **27**, 18.

⁵⁸ Compare J. Joly, *Radioactivity and Geology*, p. 11; H. H. Poole, *Phil. Mag.*, 1910, [vi], **19**, 314. The result is considerably higher than is to be anticipated from the simple disintegration theory.

⁵⁹ *Ann. Report*, 1906, 351; H. A. Bumstead, *Phil. Mag.*, 1908, [vi], **15**, 432; *A.*, 1908, ii, 342.

Recoil of Disintegration Products.

When an atom of mass of the order of 200 expels an α -particle of mass 4 with a velocity of the order of 2×10^9 cm. per second, it follows, if the expulsion obeys ordinary mechanical laws, that the product of the disintegration must recoil with a velocity of the order of 4×10^7 cm. per second in the direction opposite to that of the expelled α -particle. Conclusive evidence of this recoil has now been obtained, and the phenomenon, in addition, has been the means of adding an extremely valuable new method for the separation of radioactive products, too difficult to be effected by ordinary chemical and physical processes. In the last Report, attention was directed to the feeble residual activity left after the active deposit of actinium produced by the actinium emanation completely decays, which was described as one of the most interesting radioactive phenomena of the time.⁶⁰

With very active preparations of radio-actinium this activity has been further studied, and it has been shown to be due to actinium-*X*, which is the parent rather than the product of the active deposit. Now actinium-*X* is not volatile even at a red-heat. The residual activity is completely prevented when the actinium preparation is wrapped in tissue paper, which allows the emanation to go through, and the ordinary active deposit of actinium to be formed without hindrance. Actinium-*X*, free from its parent radio-actinium, does not show the residual activity, although, of course, it generates emanation, and produces the ordinary active deposit. The explanation is that it is only produced by nascent actinium-*X*, which recoils from the actinium preparation at the moment of its formation from radio-actinium by the expulsion of the α - and β -particles.⁶¹

It is found that a negative charge on the plate being made active increases greatly the amount of recoiled actinium-*X* collected. In the case of a long known similar phenomenon with radium-*B*,⁶² which is not "volatile" in the ordinary sense, but appears so at the moment of its formation from radium-*A* by expulsion of an α -particle, the recoil explanation had already been suggested. This case and many others⁶³ has been reinvestigated, and been found parallel to that of actinium-*X*, the amount of radium-*B* collected being greatly assisted if the collecting surface is negatively charged with respect to the active deposit. It appears that the recoiled

⁶⁰ *Ann. Report*, 1907, 328.

⁶¹ O. Hahn, *Physikal. Zeitsch.*, 1909, **10**, 81; *A.*, ii, 206.

⁶² Miss Brooks, see Rutherford's *Radioactivity*, 2nd edition, p. 392.

⁶³ O. Hahn and L. Meitner, *Ber. Deut. physikal. Ges.*, 1909, **11**, 55.

product of disintegration carries a positive charge, as it has been found to do in other cases. In the actinium active deposit itself, it is known that the first substance, actinium-*A* (half-period, thirty-six minutes), only expels feeble β -radiation and no α -radiation, whereas the product, actinium-*B*, expels an α -particle (possibly two in rapid succession)⁶⁴ in its rapid change (half-period, 2.15 minutes) into actinium-*C*. This latter substance, which had been discovered shortly before these experiments, as it is separated from a solution of the active deposit by adsorption with charcoal and finely divided metals,⁶⁵ gives only the penetrating β - and γ -rays of actinium, and has a half-period of 5.1 minutes. It was found that pure actinium-*C*, decaying exponentially to zero with a period of 5.1 minutes, and giving only β - and γ -radiation, could be obtained by exposing a negatively charged surface in the neighbourhood of the active deposit. In suitable circumstances, more than half the theoretical production of pure actinium-*C* could be got in this way. In these rapid successive changes the new method of separation is a most powerful new weapon of attack. Changes too rapid for any other process to be of service can thus be detected. The next result was new. Thorium-*A* (half-period, 10.6 hours) gives no α -particle whereas the product thorium (*B* and *C*) (half-period, 60.4 minutes⁶⁶ gives two of different range, and it was previously thought the β - and γ -rays also. The recoil method, however, yielded from the thorium active deposit an entirely new product, called thorium-*D*, giving only the β - and γ -rays, decaying exponentially to zero with half-period 3.1 minutes. It gave no α -rays on decaying, and hence must follow thorium (*B* and *C*) in the series. The absorption curves of the thorium-*D* β -rays are identical with those of the more penetrating of the two types given by the thorium active deposit. An independent set of similar experiments, carried out with a condensed film of radium emanation in a vacuum,⁶⁷ showed that radium-*A*, -*B*, and -*C* recoiled from the emanation. No electric field was employed in these experiments, and it was found that the amount recoiled varied inversely as the square of the distance, and was very markedly diminished by the presence of air or other gases. The air absorbed the products recoiled exponentially, and in one case, under 0.44 mm. pressure with 6.5 cm. of path, half was absorbed by the air. Hydrogen was found to absorb the recoil products far more than air in proportion to its density.

In both sets of investigation it was established that the expulsion of the β -particle by itself produces a detectable recoil of the

⁶⁴ Compare Mlle. Blanquies, p. 236.

⁶⁵ O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1908, **9**, 649; *A.*, 1908, ii, 920.

⁶⁶ *Ann. Report*, 1906, 342.

⁶⁷ S. Russ and W. Makower, *Proc. Roy. Soc.*, 1909, **82**, A, 205; *A.*, ii, 455.

product, which is far smaller than that produced by the α -particle. Thus, the active deposit of radium, after being left long enough for the rapidly changing α -ray substance, radium-*A*, completely to disintegrate, exposed in a vacuum gave a recoil product of radium-*C* alone, which could only be due to the β -particle expelled in the change of radium-*B*. Further investigations have established that radium-*C* itself gives a new rapidly decaying recoil product.⁶⁸ The complex nature of radium-*C* has already been adumbrated on several grounds.⁶⁹ In addition to the evidence drawn from the very penetrating character of the α -radiation, which indicates a far more rapidly changing product than that ascribed to radium-*C* (half-period, 19 minutes), and to the discrepancies between the calculated periods of radium-*D*, the substance gives a complex β -radiation not exponentially absorbed by aluminium (compare p. 240). Recoil experiments with pure radium-*C* itself, separated by chemical methods from a solution of the active deposit of radium, gave products decaying very rapidly, with a half-period of from 1 to 2.5 minutes. Only very feeble recoil effects were obtained, indicating that radium-*C*₁ gives β -rays and no α -rays. The recoil product, radium-*C*₂, gave α -rays, and decayed exponentially with a period of about two minutes.

There is thus evidence that radium-*C* is complex and consists of two rapidly succeeding products, whilst three are suggested. The results so far, however, are not very conclusive. The new method may perhaps also apply to cases like radium-*F*, to determine whether it is the true end-product of the series. There is little doubt that the new method may serve to throw light on problems capable of being attacked in no other way.⁷⁰ There is some evidence that radium-*F* gives a recoil product which carries a positive charge, and is detectable thereby. If so, a method may exist for the recognition of the final end-product of the series, even although it is completely non-radioactive. Even the determination of the atomic weight by measurements of the magnetic and electric deflexion of the charged particle is not entirely out of the question.

Influence of Temperature on Radioactive Change.

This subject has been left in an unsatisfactory state in previous reports, and, in spite of further researches, still remains unsettled, a real conflict existing in the experimental results of different workers, and even of the same workers in different experiments.

⁶⁸ O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1909, **10**, 697; *A.*, ii, 849.

⁶⁹ *Ann. Report*, 1907, 312 and 338.

⁷⁰ J. C. McLennan, *Nature*, 1909, **80**, 490; compare also E. Aschkinass, *Ann. Physik*, 1908, [iv], **27**, 377; *A.*, 1908, ii, 920.

Many of the results already recorded⁷¹ have been independently confirmed.⁷² The β - and γ -activity of radium-*C* from a quartz tube containing the radium active deposit has now been measured during the actual heating. Soon after heating to 1100° or 1200°, a decay more rapid than the normal occurred, gradually becoming normal as the heating was maintained. On cooling, the decay was at first less than, but increased to, the normal. Disturbances due to unequal volatilisation of the products and to the permeability of the tube at high temperature appear to have been eliminated. With the emanation itself in the quartz tube, a rapid increase at first was always observed. In the first experiments, cooling brought the activity below the normal, and the activity then gradually increased to the normal. In later experiments, however, this increase was not observed. This was attributed to non-homogeneity of the emanation, for which some other as yet incomplete evidence exists, the consideration of which may profitably be postponed.⁷³ With the hard γ -rays little change was observed. It is concluded that the changes both of the emanation and radium-*A* are accelerated by rise of temperature. Other investigators continue to deny any effect of temperature.⁷⁴ The changes, in any case, are small, but the evidence in their favour cannot be altogether ignored. The question remains an open one.

Helium and Ultimate Disintegration Products.

A measurement of the rate of production of helium from 0.07 gram of radium chloride, by absorbing condensable gases in charcoal cooled in liquid air (sometimes in liquid hydrogen), and measuring the increase in the amount of residual gas in a compression gauge, gave 0.37 cu. mm. of helium per gram of radium per day, which is very nearly the theoretical value (compare p. 235).⁷⁵ The radium was heated to 450° before the measurements, and the purity of the gas measured as helium was established. The production of infinitesimal quantities of helium from uranium and thorium has been established by direct experiments with large quantities of materials by means of the calcium absorption process, which ensures that the helium could not have been of atmospheric

⁷¹ *Ann. Report*, 1907, 336.

⁷² W. Engler, *Ann. Physik*, 1908, [iv], **26**, 518; *A.*, 1908, ii, 650.

⁷³ Compare also Rutherford and Tuomikoski, *Mem. Manchester Phil. Soc.*, 1909, **53**, xii.; *A.*, ii, 456; Rutherford, *Phil. Mag.*, [vi], 1909, **17**, 723; *A.*, ii, 456; A. Debierne, *Compt. rend.*, 1909, **148**, 1264; *A.*, ii, 534.

⁷⁴ H. W. Schmidt, *Physikal. Zeitsch.*, 1908, **9**, 113; *A.*, 1908, ii, 141; Makower and Russ (controversial against the latter), *ibid.*, 250; *A.*, 1908, ii, 449; H. W. Schmidt and P. Cermak, *ibid.*, 816.

⁷⁵ Sir J. Dewar, *Proc. Roy. Soc.*, 1908, **81**, A, 280; *A.*, 1908, ii, 921.

origin. The amount produced in both cases is of the same order as the theoretical. In the uranium experiments a spectroscopic estimation of the rate of production agreed with the theoretical on the assumption that each atom of uranium disintegrating gives one, not two, atoms of helium, but the estimate is necessarily a minimum one.⁷⁶ The amount corresponds with only 11 cu. mm. per thousand kilograms of uranium per year.

Attempts have been made to use the amount of helium contained in common rocks and minerals as a criterion of their geological age. Except in the one definite case of beryl, which contains a marked amount of helium and practically no radioactive matter, and possibly of the saline minerals, such as carnallite, the amounts of helium correspond roughly with what is to be expected from the amount of uranium (measured as radium) and thorium.⁷⁷ It has been established, however, that under laboratory conditions the rate of escape of helium, even from dense, compact minerals like thorianite, far exceeds the possible rate of production, so that the primitive natural conditions must have been more favourable to the retention of helium.⁷⁸ This escape, of course, would invalidate the estimation of geological age, making it too low. However, the most recent results with hæmatites of various geological horizons, from Oligocene to Devonian, indicate ages far greater than are usually ascribed by geologists.⁷⁹ Still more recent results with zircons of geological ages from Tertiary to Archean, indicate a very close agreement between the age and the ratio of helium to radioactive matter. Doubt has been thrown on the existence of argon in zirconium minerals, such as malacone, except in spectroscopic quantities.⁸⁰ Doubt has also been thrown on the possibility of lead being the ultimate product of the uranium disintegration,⁸¹ owing to the absence (less than 0.01 per cent.) of lead in a fine crystal of autunite (hydrated uranium calcium phosphate). Independent spectroscopic examination of another specimen of this mineral, it is true, and on Cornish tobernite (hydrated uranium copper phosphate), showed lead as the only

⁷⁶ F. Soddy, *Phil. Mag.*, 1908, [vi], **16**, 513; *A.*, 1908, ii, 921; *Physikal. Zeitsch.*, 1909, **10**, 41; *A.*, ii, 207; *Proc. Phys. Soc.*, 1909, 178.

⁷⁷ R. J. Strutt, *Proc. Roy. Soc.*, 1908, **80**, A, 572; **81**, A, 272 and 278; *A.*, 1908, ii, 649, 922, 923; J. W. Waters, *Phil. Mag.*, 1909, [vi], **18**, 677; *A.*, ii, 848.

⁷⁸ R. J. Strutt, *Proc. Roy. Soc.*, 1909, **82**, A, 166; *A.*, ii, 457; J. A. Gray, *ibid.*, 301; *A.*, ii, 570.

⁷⁹ R. J. Strutt, *ibid.*, 1909, **83**, A, 97; *A.*, 1910, ii, 9; *ibid.*, meeting of 9/12/09, abstract only available.

⁸⁰ R. J. Strutt, *ibid.*, 1908, **80**, A, 572; *A.*, 1908, ii, 649; C. F. Hogley, *Phil. Mag.*, 1909, [vi], **18**, 672; *A.*, ii, 884; A. von Antropoff, *Zeitsch. Elektrochem.*, 1908, **14**, 585; *A.*, 1908, ii, 943.

⁸¹ W. Marckwald and B. Keetman, *Ber.*, 1908, **41**, 49; *A.*, 1908, ii, 144.

important foreign constituent. The quantity in the first case was, however, only such as would be formed theoretically in 10,000 years.⁸² The mineral must either be of extremely recent formation, or lead cannot be the ultimate product. With regard to the ultimate product of the thorium series, the active deposit of thorium appears to decay away completely, leaving no feeble residual activity, and the unknown product of the last known member, thorium-*D*, if not entirely stable, must possess a life period of at least two million years.⁸³ In this research the periods of thorium-*A* and -*B* were redetermined very accurately, and found to be 10·605 hours and 60·4 minutes respectively.

The Radioactive Emanations.

Physical Properties of Radium Emanation.—Several workers now having a considerable fraction of a gram of pure radium, many investigations have been carried out on the properties of pure radium emanation. The volume of the emanation in equilibrium with 1 gram of radium has been found to be almost exactly that theoretically deduced (p. 235) on the assumption that one monatomic molecule of emanation results per atom of radium disintegrating, the most trustworthy measurements agreeing in giving about 0·58 to 0·6 cu. mm. at N.T.P. The initial rapid contraction of volume of freshly separated emanation, although not entirely explained, has been traced to impurities, which have in no case been entirely eliminated. The measurements have therefore been taken of the minimum volume reached after a few hours. The amount of emanation measured has been compared by γ -ray measurements with a standard radium preparation.⁸⁴ The volume of emanation has been proved to be proportional to its γ -activity, independently of the time of its accumulation.

On this infinitesimal quantity of gas, determinations have been made of the spectrum, vapour pressure, boiling point, freezing point, critical temperature, critical pressure, and the density of the liquid. The spectrum⁸⁵ is now fairly well known, having been photographed both with the prism and grating with sufficiently concordant results. An unexplained fact is the presence of xenon

⁸² J. A. Gray, *Phil. Mag.*, 1909, [vi], **18**, 816 and 937; *A.*, ii, 956.

⁸³ F. v. Lerch, *Sitzungsber. K. Akad. Wiss. Wien.*, 1907, **116**, (iia), 1443.

⁸⁴ E. Rutherford, *Phil. Mag.*, 1908, [vi], **16**, 300; *A.*, 1908, ii, 791; R. W. Gray and Sir W. Ramsay, *Trans.*, 1909, **95**, 1073; A. Debierne, *Compt. rend.*, 1909, **148**, 1264; *A.*, ii, 534.

⁸⁵ E. Rutherford and T. Royds, *Phil. Mag.*, 1908, [vi], **16**, 313; *A.*, 1908, ii, 787; T. Royds, *ibid.*, 1909, [vi], **17**, 202; *A.*, ii, 206; A. T. Cameron and Sir W. Ramsay, *Proc. Roy. Soc.*, 1908, **81**, A, 210; *A.*, 1908, ii, 786; T. Royds, *ibid.*, 1909, **82**, A, 22; *A.*, ii, 287; H. E. Watson, *ibid.*, 1909, **83**, A, 50; *A.*, ii, 954.

in the emanation spectrum on one occasion, for which no source has been suggested. The vapour-pressure curve of the emanation has been plotted in one set of investigations from 500 mm., 202.6° Abs. (solid) to 47,450 mm., 377.50° Abs. (critical temperature), the freezing point being given at -71° .⁸⁶ The liquid emanation observed in a microscope is described as at first colourless and transparent like water, but as its temperature is reduced it ceases to transmit light, and on further cooling with liquid air the solid emanation glows with great brilliancy, at first like a small steel-blue arc lamp, whilst at a still lower temperature the glow is a brilliant orange-red. From a comparison of its boiling point, critical temperature, and critical pressure with those of the other inert gases, it was concluded that the atomic weight of the emanation was 176. The theoretical value, on the assumption that only an α -particle is expelled in the production of the emanation from radium, is 222.5, which has also been advocated from the same data on other grounds.⁸⁷ Both numbers would fit in the Periodic Table equally well. Before this evidence from the physical constants can be considered beyond criticism, it would be of interest to have similar measurements carried out with 0.1 cu. mm. of xenon, krypton, and argon.

Diffusion-Coefficients.—The coefficients of diffusion of all three emanations have been redetermined with considerable accuracy, but the deduction therefrom of the molecular weight of the emanation appears to be beset with uncertainty. In the first place, the effect of a charge on the molecule, which at least initially it may reasonably be supposed to have, has been considered to be a disturbing factor sufficient completely to vitiate the method and to give too low values for the molecular weight.⁸⁸ Possibly another disturbing factor, which also would apply mainly to the short-lived emanations, is the effect of recoil, causing the emanation molecule at first to move more rapidly than that of an ordinary gas of similar molecular weight and temperature. For the long-lived radium emanation, however, one would not expect either objection to apply, unless, indeed, the emanation molecule has its charge maintained by the ions in the gas. It has been suggested that fresh evidence might be obtained from a comparison of the thermal conductivities of the emanation and the heavier argon gases at very low pressure,⁸⁹

⁸⁶ R. W. Gray and Sir W. Ramsay, *loc. cit.*; compare also E. Rutherford, *Phil. Mag.*, 1909, [vi], 17, 723; *A.*, ii, 456.

⁸⁷ G. Rudolf, *Zeitsch. Elektrochem.*, 1909, 15, 749; *A.*, ii, 954.

⁸⁸ Sir J. J. Thomson, Camb. Phil. Society's Meeting, 8/11/09. Abstract only so far available.

⁸⁹ F. Soddy and A. J. Berry, Royal Soc. Meeting, 9/12/09; F. Soddy, *Nature*, 16/12/09.

which have been shown with argon and neon to agree fairly well with the values calculated from the kinetic theory.

The most notable experimental advance with the radium emanation has been the direct comparison of its velocity of diffusion in hydrogen through asbestos plugs with that of mercury vapour at 250° and 275° . This is the first time direct comparison has been made with a monatomic gas of similar molecular weight.⁹⁰ The coefficients of diffusion of the emanation at the two temperatures were 0.0341 and 0.0376, as compared with 0.0370 and 0.0407 for mercury. On the assumption that the molecular weights are proportional to the squares of the diffusion-coefficients, the molecular weight of the emanation is 234.5. Another determination⁹¹ in air at the ordinary temperature has been made by Curie and Danne's original method, with improvements, by measuring the exponential escape of emanation from a bulb provided with a long, narrow tube. This gave the coefficient of diffusion 0.1015 at N.T.P. If the same law holds for the emanation as for hydrogen, water, and carbon dioxide, the molecular weight would be between 70 and 100, but no monatomic gas seems to have had its coefficient of diffusion so measured. The coefficient of diffusion of the actinium emanation has been deduced from the exponential decrease, with height, of the active deposit on a vertical wire in a long cylinder, at the bottom of which an actinium preparation was spread.⁹² Also the rate of diffusion of actinium and thorium emanations have been compared by the same method.⁹³ In the first investigation the coefficient was determined in air at various pressures, and in carbon dioxide and hydrogen. It was found that the ratios of the diffusion-coefficients in air to those in hydrogen and carbon dioxide respectively were the same for the actinium emanation as for ether, alcohol, water, etc. It was concluded that the molecular weight must be about 70 whatever the conditions under which diffusion is measured. In the second investigation, the values found for the actinium emanation agreed well with those calculated by Graham's law from the diffusion-coefficients in air when diffusion was carried out in hydrogen, carbon dioxide, sulphur dioxide, and argon. The actinium emanation coefficient was 1.19 times that of the thorium emanation (in air at 76 cm.), and it was concluded that the molecular weight of the thorium emanation is 1.42 times that of actinium. This question of the molecular weights of the emanation is thus still far from settled, and is one of the greatest importance in the present state of the subject.

⁹⁰ P. B. Perkins, *Amer. J. Sci.*, 1908, [iv], **25**, 461; *A.*, 1908, ii, 552.

⁹¹ L. Chaumont, *Le Radium*, 1909, **6**, 106; *A.*, ii, 781.

⁹² C. Bruhat, *Compt. rend.*, 1909, **148**, 629; *Le Radium*, 1909, **6**, 67; *A.*, ii, 300.

⁹³ S. Russ, *Phil. Mag.*, 1909, [vi], **17**, 412; *A.*, ii, 366.

Condensation.—An interesting, but somewhat incomplete, investigation⁹⁴ has shown that whereas the temperature of condensation of the radium emanation in tubes of copper, iron, tin, and silver is about the same (-155°) as that originally found, in glass the temperature is about 20° lower. In silvered glass the temperature was little, if any, higher than in ordinary glass. This may explain the differences between the initial experiments, in which it was found that the temperature of condensation (in metal tubes) was extremely sharp, and those of a large number of later investigators (working with glass apparatus), who have found that by continued pumping some emanation can be continuously extracted even when it is kept at liquid-air temperature. Investigations have also been carried out on the absorption of the emanations by charcoal and other porous materials.⁹⁵ Not much hitherto has been known of the condensation of the actinium emanation, as its rapid decay (to 1/2 per cent. in 30 seconds) makes the experimental work difficult. A very complete and careful comparison⁹⁶ has now been made between its behaviour at low temperature and that of the thorium emanation, with the notable result that the two emanations are so completely alike as regards their condensation that they can barely be distinguished. This is unexpected in view of large difference in molecular weight indicated by diffusion experiments. At -120° both emanations begin to condense, and condensation is complete at -150° . If anything, the actinium emanation is slightly the more volatile. The disengagement of the emanation from radium-barium chloride and fluoride has been further studied in great detail. In the case of the former, the temporary minimum of emanating power passed through at 920° , 25° below the melting point, has been associated with a point of polymorphic transformation.⁹⁷ Radium salts precipitated along with hydrates of the rare earths have a very strong emanating power in the cold in the dry state, as in the case of the actinium preparations.⁹⁸ The great loss of emanation from dry radium bromide in the cold, as compared, for example, with radium chloride, is perhaps to be ascribed to the greater spontaneous instability of the bromide, and its rapid conversion into hydroxide and carbonate by the action of the air.

The Question of Transmutational Reactions Produced by the

⁹⁴ A. Laborde, *Le Radium*, 1909, **6**, 289; *A.*, ii, 634.

⁹⁵ Compare also E. Henriot, *ibid.*, 1908, **5**, 41; *A.*, 1908, ii, 651; R. W. Boyle, *Phil. Mag.*, 1909, [vi], **17**, 374. (See *A.*, 1908, ii, 1005.)

⁹⁶ S. Kinoshita, *ibid.*, 1908, [vi], **16**, 121; *A.*, 1908, ii, 652.

⁹⁷ *Ann. Report*, 1907, 332; L. Kolowrat, *Le Radium*, 1909, **6**, 321; *A.*, 1910, ii, 91.

⁹⁸ H. Herschinkel, *Compt. rend.*, 1909, **149**, 275; *A.*, ii, 714.

Radium Emanation.—The experiments on the presence of neon with helium in the gases produced by the action of radium emanation upon liquid water⁹⁹ have been repeated by the original investigators, who conclude that they furnish conclusive evidence of the first observed case of transmutation.¹ In the experiment described, the analysis given showed that nearly 0.3 c.c. of nitrogen gas was present. Other workers have carried out similar experiments, and obtained in four out of five experiments no indication of neon in the helium produced. It was found that when 1/10 c.c. of air was added to the helium, and the gas again subjected to cold charcoal, the neon spectrum could be clearly seen. In the fifth experiment neon was observed, which was ascribed to atmospheric origin through air leakage.² The presence of lithium in salts of copper, subjected to the action of the radium emanation, was not observed in a series of independent experiments carried out with very carefully purified materials in platinum vessels.³ It was shown that water originally free from lithium, after standing in glass vessels for a short time, contained it in detectable quantities. The presence of lithium in opaque and transparent fused quartz was also detected. The occurrence of lithium in radioactive minerals has been examined. Lithium in spectroscopic quantity was found in all, but no relation existed between the amount of lithium and that of copper. Autunite contains no copper, and carnotite but little copper, and relatively much lithium.⁴ Experiments to detect lithium after the direct action of the rays and emanation of radium on salts of copper and gold have given negative results.⁵

The formation of considerable quantities of carbon dioxide by the action of carbon dioxide-free radium emanation on solutions of hydrofluosilicic acid, titanium sulphate, zirconium nitrate, thorium nitrate, and lead chlorate, and its absence in similar experiments with mercurous nitrate, has been interpreted on the view that the elements of the carbon group are degraded into carbon by the action of the emanation, the more readily (except lead) the higher the atomic weight of the element.⁶ From the thorium solution, 2.9 milligrams of carbon, as carbon dioxide, were obtained per cu. mm. of emanation employed.

⁹⁹ *Ann. Report*, 1907, 335.

¹ Sir W. Ramsay and A. T. Cameron, *Trans.*, 1908, **93**, 992.

² E. Rutherford and T. Royds, *Phil. Mag.*, 1908, [vi], **16**, 812; *A.*, 1908, ii, 1006.

³ Mme. Curie and Mlle. Gleditsch, *Compt. rend.*, 1908, **147**, 345; *A.*, 1908, ii, 793.

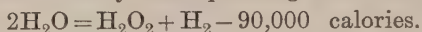
⁴ Mlle. Gleditsch, *ibid.*, **146**, 331; *A.*, 1908, ii, 246; Sir W. Ramsay and A. T. Cameron, *ibid.*, 456; *A.*, 1908, ii, 247.

⁵ E. P. Perman, *Trans.*, 1908, **93**, 1775.

⁶ Sir W. Ramsay and F. L. Usher, *Ber.*, 1909, **42**, 2930; *A.*, ii, 850.

The Radioactive Decomposition of Water and Various Gases.

For six or seven years the source of the excess of hydrogen always present in the electrolytic gas evolved in the radioactive decomposition of water has remained unaccounted for, but much fresh light has recently been thrown on the question. Contrary to earlier observations, the decomposition of water by the penetrating rays only of a considerable quantity of radium has been observed.⁷ After the first three days, for some months, a steady evolution of gas occurred, followed by a slow progressive diminution in the rate of production. The steady evolution was 0.115 c.c. per day per gram of radium, which is about 1 per cent. of the amount evolved from radium in solution. On testing the gas, it was found to be pure hydrogen, and an amount of hydrogen peroxide was found in the water nearly corresponding with the equation :



It is calculated that rather more than 0.01 per cent. of the total energy evolved by the radium can be utilised in this reaction. No such effect was observed for X-rays, but ultraviolet light from a quartz mercury vapour lamp brings about the same reaction. This is in conformity with the observation that hydrogen peroxide is found in greater amount in snow and rain during the daytime than at night, and that it is not found in dew.

An unaccountable cessation in the normal evolution of hydrogen and oxygen from a solution containing more than 0.2 gram of radium has been recorded. After some months of normal gas evolution, very little gas was generated for two months, and then the normal rate of evolution (25 c.c. per week) was resumed and maintained.⁸ As a result of a long series of experiments on the chemical action of the radium emanation on water, mixtures of hydrogen and oxygen, both moist and dry, oxides of carbon, hydrogen chloride, ammonia, and mixtures of nitrogen and hydrogen, it was found that the general law could be formulated that each molecule of emanation disintegrating produces a definite effect. The volume changes in the gases brought about by the presence of a definite quantity of emanation proceed exponentially with the time, the constant, for the average of all the experiments, being the same as that of the decay of the radium emanation.⁹ Liquid water is decomposed, whereas the mixed gases, hydrogen

⁷ A. Debierne, *Compt. rend.*, 1909, **148**, 703; *Le Radium*, 1909, **6**, 65; *A.*, ii, 364; M. Kernlaum, *Compt. rend.*, 1909, **148**, 705; **149**, 116 and 273; *Le Radium*, 1909, **6**, 225; *A.*, ii, 364, 714, 717.

⁸ R. W. Gray and Sir W. Ramsay, *Trans.*, 1909, **95**, 1073.

⁹ Sir W. Ramsay and A. T. Cameron, *ibid.*, 1908, **93**, 966; compare also H. Herschfinkel, *Le Radium*, 1909, **6**, 228. (See *A.*, ii, 778.)

and oxygen, in presence of phosphoric oxide are recombined. Carbon dioxide is decomposed with deposition of carbon and formation of carbon monoxide, whilst the latter gas also deposits carbon and forms carbon dioxide and some oxygen. Hydrogen chloride and ammonia are decomposed into their constituents, whilst mixtures of nitrogen and hydrogen contract in presence of fused calcium chloride, which absorbs ammonia. At 130° mixtures of hydrogen and oxygen recombine, whereas the reverse change with steam did not appear to take place. The general action of radioactive substance in causing chemical combination appears to be well explained by dissociation of molecular aggregates, and the temporary formation of free atoms, rendering the substances extremely reactive, as in the so-called nascent state. This great chemical reactivity of otherwise inert substances in presence of the radioactive materials has always to be remembered in the interpretation of their actions.

The Active Deposits.

The conditions of the deposition of the active deposit, with and without the action of electric fields, and of gravity¹⁰ have been examined in great detail. The amount of active deposit attracted to the negative electrode in the radium emanation varies with the voltage in a manner closely analogous to the ionisation current through the gas, indicating that the specific velocity and coefficient of recombination is of the same order of magnitude for the active matter as for the ions in the gas. Hence the practically important result follows that to get the maximum deposition a voltage sufficient to produce saturation in the gas is necessary in each case.¹¹ Without the action of an electric field or gravity, by working with vertical parallel plates at varying distances apart, a maximum distance apart exists beyond which the amount of active deposit does not increase, indicating that the time taken for the particles to diffuse to the plates exceeds their period of average life. This limiting distance apart, however, is attained at a distance twelve times less than indicated by theoretical considerations, as though the particles of the active products were aggregations very much larger than single molecules.¹² It has been established that radium-A is absent from that part of the active deposit falling under gravity, the time taken in falling being greater than the short life-period of this substance. This was done very neatly by exposing two horizontal superimposed

¹⁰ *Ann. Report*, 1907, 336.

¹¹ H. W. Schmidt, *Physikal. Zeitsch.*, 1908, 9, 184.

¹² A. Debierne, *Le Radium*, 1909, 6, 97.

plates to the emanation, and then, after the removal of the plates from the emanation, balancing the ionising current from the under surface of the upper plate against that due to the upper surface of the lower plate. The net effect was due to the gravity-deposited activity alone, and its decay curve showed no rapid initial drop characteristic of radium-*A*.¹³ By finding the maximum distance between the plates beyond which the gravity-deposited activity did not further increase, the time of fall and, from Stokes' law, the size of the falling particle were estimated. In moisture-laden air, the size found was much greater than in dry, and reached diameters from 150 to 280 $\mu\mu$, which is well within the region of ultramicroscopic vision. Supporting this inference, the formation of persistent mists has been observed in flasks containing moist, but not necessarily saturated, air illuminated by the arc. These last sometimes over a month, and gradually disappear as the emanation decays. They have been traced to chemical actions, such as the formation of oxides of nitrogen from the air, and the oxidation of sulphur from india-rubber stoppers, and are especially dense in chemically reactive gases such as chlorine.¹⁴ The results seem to have a bearing on the importance of radioactivity in producing meteorological phenomena. By experiments on the activity deposited on rods immersed in the emanation at various temperatures, it has been found that at 900° neither radium-*A* nor -*B* will deposit, whereas radium-*C* will, and, since the deposition under these conditions is uninfluenced by the electric field, it is concluded that radium-*C* is not charged at the moment of its formation from radium-*B*. The following volatilisation points are given: radium-*A*, 900°; radium-*B*, 600°; radium-*C*, 1200°.¹⁵ A full comparison of the behaviour of the active deposits from the three emanations in an electric field in gases at various pressures has been carried out.¹⁶ The conclusion is come to that some of the particles of the active deposit carry *negative* charges, for, especially in the case of actinium, some of the deposit is attracted to the positive electrode. It appears that the sign of the charge on the particle depends to some extent on the number of collisions made with the gas molecules and may be either positive or negative. Recoil phenomena probably play a part in the interpretation of some of the observed effects.

¹³ L. Wertenstein, *Compt. rend.*, 1909, **149**, 268; *A.*, ii, 713.

¹⁴ Mm. Curie, *ibid.*, 1908, **147**, 379; *A.*, 1908, ii, 797; H. Herschfinkel, *Le Radium*, 1909, **6**, 228.

¹⁵ W. Makower, *Le Radium*, 1909, **6**, 50.

¹⁶ S. Russ, *Phil. Mag.*, 1908, [vi], **15**, 601 and 737; *A.*, 1908, ii, 552, 556; W. T. Kennedy, *ibid.*, 1909, [vi], **18**, 744; *A.*, ii, 955.

The Uranium-Radium Disintegration Series.

Uranium Minerals.—A valuable set of measurements, giving the relative α -ray ionisation due to each member of the uranium-radium disintegration in equilibrium in radioactive minerals, in terms of that given by the parent substance, uranium, as unity, is embodied in the following table ¹⁷:

Uranium.....	1·00	Radium- <i>B</i>	0·04 (?)
Ionium	0·34	Radium- <i>C</i>	0·91
Radium	0·45	Radium- <i>F</i>	0·46
Radium emanation	0·62	Actinium and products..	0·28
Radium- <i>A</i>	0·54		
Total activity.....		4·64 times uranium	

Omitting radium-*B*, the activity of which is due to very soft β -rays, the actinium products, and uranium itself, the numbers are in good agreement, considering the ranges of the various α -particles expelled, with what is to be expected if each product gives one α -particle per atom disintegrating. But the results indicate clearly that uranium gives slightly more effect than would be the case if two α -particles were expelled. It is not impossible that in uranium two α -ray changes may succeed each other too rapidly for analysis. But as the range of the α -particles of uranium is low, this is not very probable. It is more likely, if two successive changes are really involved, that complete chemical similarity between the uranium and its product has hitherto prevented their separate identification (compare footnote, p. 262). Be that as it may, the result bears out in a most striking manner the atomic weight relations existing between uranium and radium, for the difference of 12 units indicates that three α -particles are expelled in the course of the transformation. Since ionium, the direct parent of radium, gives an α -particle, this requirement is entirely satisfied.

In the case of actinium and its products, for which the data are rather uncertain owing to the difficulties in completely separating it from the mineral, it is clear the result is quite exceptional. In the actinium series, four successive changes, possibly five, in which α -particles of average range are expelled, are known to occur. This result is the chief reason for considering actinium to be not in the main uranium-radium series, but in a branch or subsidiary series from uranium. The results would be consistent if out of about every eight atoms of uranium disintegrating seven produced radium and one actinium. The hypothesis has been put forward ¹⁸

¹⁷ B. Boltwood, *Amer. J. Sci.*, 1808, [iv], 25, 269; *A.*, 1908, ii, 454; H. N. McCoy and W. H. Ross, *J. Amer. Chem. Soc.*, 1907, 29, 1698; *A.*, 1908, ii, 80.

¹⁸ H. N. McCoy and W. H. Ross, *ibid.*, 1698; *A.*, 1908, ii, 80; F. Soddy, *Phil. Mag.*, 1909, [vi], 18, 739; *A.*, ii, 952.

that the same atom may disintegrate in more than one way, each mode obeying the simple law independently of the other mode of disintegration. This would be extremely difficult to establish by experiment, for were one type of rays (say α -rays) given out in one mode of disintegration and another (say β -rays) in another, each radiation would decay with the *same* period, which would be the sum of two separate periods. The same fixed proportion would, however, exist between the amounts of products of the two modes of disintegration as existed between the reciprocals of the separate periods. Thus, if at one point in the disintegration series, one of the products disintegrated in dual fashion, the period of the one mode in which actinium was the product being about seven times the period of the other mode which gave rise to radium, the known relations between actinium, radium, and uranium would receive an easy explanation.

Doubt has been cast upon the complete constancy of ratio between the quantities of radium and uranium in minerals.¹⁹ This ratio has been redetermined by separating the two constituents chemically. For autunite a relatively smaller number (2.85), and for thorianite a relatively larger number (4.19), was obtained than the value for Joachimsthal pitchblende, which agreed with the accepted value (3.58×10^{-7}). It appears that the ratio is the higher the older the mineral, although the differences are not great. It would be interesting to have also measurements of the radium, for comparison, in the same minerals not subjected to any chemical processes of separation.

It is to be noted that the anomalous uranium-free radium mineral from Issy l'Éveque, the radium of which appears to have been derived from a distant uranium-lode by the action of percolating water, has its activity, which in the lump exceeds that of pure pitchblende, entirely confined to the surface. Acids dissolved off practically all the activity, but hardly any of the mineral itself.²⁰

As convenient standards of radioactivity have been suggested films of pure uranium oxide, U_3O_8 (about 0.7 gram, spread uniformly over a circular plate 7 cm. in diameter by means of chloroform), for which the α -activity is the maximum. The total α -activity of 1 gram of uranium, that is, the activity in a practically infinitely thin film, if no absorption occurred in the substance or its support, is equal to that of 796 sq. cm. of such a film. The saturation current per sq. cm. of surface of these films

¹⁹ Mlle. Gleditsch, *Compt. rend.*, 1909, **148**, 1451; **149**, 267; *Le Radium*, 1909, **6**, 165; *A.*, ii, 533, 714.

²⁰ H. N. McCoy and W. H. Ross, *J. Amer. Chem. Soc.*, 1907, **29**, 1698; *A.*, 1908, ii, 80.

is 5.79×10^{-13} ampere. They can thus be used to calibrate the readings of electroscopes in absolute measure. The α -activity of pure radium, free from products, is given as 1.3×10^6 times that of equal weight of uranium.²¹

The manufacturers' designation of the activity of radium preparations, as so many million times uranium, are meaningless and misleading. The best method is to compare the γ -activity of a known weight of the radium sample against a known weight of a standard preparation, under identical conditions, both preparations having been kept sealed up in glass tubes (provided with platinum wires sealed through) for at least a month. The purity of the primary standard should be checked by atomic weight estimations, or by the rate of evolution of heat. The ready spontaneous decomposition of radium bromide must be borne in mind.²² A specimen initially of 0.5 gram of pure radium bromide, as prepared by the maker, was found on delivery to weigh only 0.388 gram, and to be partly insoluble in water, but soluble in hydrobromic acid with evolution of carbon dioxide and gain of weight. Afterwards for some months the solution evolved bromine and relatively little oxygen. Then the evolution of bromine stopped, and the normal evolution of electrolytic gas began.

Radio-uranium.—The separation of a new substance, acting as the direct parent of uranium-X, and therefore intermediate between it and uranium, has been described.²³ In preparing uranium-X from a large quantity of uranyl nitrate, it was noticed that in one preparation the activity due to uranium-X had increased ten times on keeping. From this preparation uranium-X was separated, decaying at its normal rate, while the remainder generated a fresh amount of uranium-X. Very little of the substance so far has been separated, and it must resemble uranium in chemical nature very closely. The evidence, so far as it goes, is clear, but further confirmation must be awaited before the existence of the body can be regarded as established. There is no evidence whether or no it gives any specific radiation.

Uranium-X.—The repeated separation of uranium-X produced from a very large quantity of uranyl nitrate, in order to obtain evidence as to the nature of the product of its disintegration, has given results difficult to interpret on the view that this substance is intermediate between uranium and radium in the disintegration series. Were uranium-X the direct parent of ionium (which in

²¹ H. N. McCoy and G. C. Ashman, *Amer. J. Sci.*, 1908, [iv], 26, 521; *A.*, ii, 148.

²² Sir W. Ramsay, *Sitzungsber. K. Akad. Wiss. Wien.*, 1908, 117, (iia), 943; *Monatsh.*, 1908, 29, 1013; *A.*, ii, 7.

²³ J. Danne, *Compt. rend.*, 1909, 148, 337; *Le Radium*, 1909, 6, 42; *A.*, ii, 288.

turn is the direct parent of radium and gives out α -rays during the transformation), it is to be expected that as its β -radiation decayed, a very feeble α -radiation, due to the ionium produced, would grow. By deviating the β -radiation as much as possible in a strong magnetic field and working in hydrogen, experiments have been made which would suffice to detect such a growth if it had occurred at the rate indicated by theory, and these experiments have given a negative result.²⁴ Although still incomplete, they raise the question whether uranium-*X* is not in the actinium rather than in the radium series.

The absorption of uranium-*X* by charcoal has shown that, for any one initial concentration of uranium-*X*, the ratio of the concentration in the solution and in the charcoal, when equilibrium is attained, is a constant independent of the mass of the charcoal employed.²⁵ This is analogous to Henry's Law for the solution of gases in liquids. A remarkable point seems to be that the absorption is dependent upon the presence of unknown impurities in the solution, and is completely prevented by a trace of thorium sulphate.²⁶

Parent of Radium.—The growth of radium in solutions of large quantities of purified uranyl nitrate has now been established to take place, and it is found to proceed at a rate proportional to the square of the time. This indicates that there can exist only one intermediate substance in the uranium-radium series, having a life-period which is long compared with the time of the experiments.²⁷ The period of average life of this substance, which is already known to be ionium, is calculated from these experiments to be 18,500 years as a maximum. If, however, there exist new intermediate substances in the series, of life-period comparable with the time of the experiments (four years), of which there is some evidence, the calculated period referred to would be reduced.²⁸

Intensely active preparations of ionium have now been prepared

²⁴ F. Soddy, *Phil. Mag.*, 1909, [vi], **18**, 858; *A.*, 1910, ii, 10.

²⁵ A. Ritzel, *Zeitsch. physikal. Chem.*, 1909, **67**, 725; *Le Radium*, 1909, **6**, 342; *A.*, ii, 851.

²⁶ Compare B. Szilárd, *Compt. rend.*, 1909, **149**, 113; *A.*, ii, 715.

²⁷ It may be remarked that the existence of a direct intermediate product so chemically alike to the parent that its full equilibrium quantity in the latter is never diminished by any chemical operation, which is of course always probable, is not considered in this and all similar deductions. The two successive substances would act always together exactly as one substance, and it is in this sense the deduction is to be read. On the other hand, if the two substances are not consecutive but are separated by an intermediate substance chemically dissimilar, as in the thorium series, the complete chemical similarity is no insuperable barrier to their separate identification.

²⁸ F. Soddy, *Phil. Mag.*, 1908, [vi], **16**, 632; *A.*, 1908, ii, 919; 1909, **18**, 846; *A.*, 1910, ii, 10.

both by the method of adding a little thorium to the mineral and separating out the thorium and ionium together,²⁹ and by precipitating the rare earths in the mineral with hydrofluoric acid in strongly acid solution.³⁰ It has also been prepared in the technical production of radium from pitchblende residues.³¹ The poverty of the latter in ionium led to the belief that it might be almost entirely separated, during manufacture, with the uranium, but the latter investigation shows that at least some is contained in the non-uranium residues. One estimate gives 20 per cent. of the full equilibrium amount. It has been established that ionium gives α -rays of range 2.8 cm. in air. But it does not give β -rays, previous observations to the contrary³² being due to the presence of uranium-X. Ionium possesses all the good qualities which have made polonium preparations of value in experimental work, with the added advantage that its activity is practically constant. The production of radium from these preparations has been proceeding at a constant rate since observations began, which is additional evidence of the extended period of life of ionium.

Radium.—Detailed accounts of the methods employed in the technical production of radium have been published, but the principles are identical with the original ones worked out by Debierne.³³ It has been shown that no radioactive matter is lost during the roasting, or in the liquors from the precipitations.³⁴ A new and very direct method for the determination of the period of average life of radium has been worked out,³⁵ depending on the complete separation of the full equilibrium amount of ionium present in a mineral and the measurement of the fraction of the equilibrium amount of radium it generates per year. The reciprocal of this fraction is the period of average life of radium. The accuracy of the method is independent of errors in the radium standards employed, and depends only on the completeness of the separation of all the ionium in the mineral. The value ascribed by this method to the period of average life was 2874 years, or for the period of half-change about 2000 years. This, which is necessarily, if anything, too high rather than too low,

²⁹ B. Boltwood, *Amer. J. Sci.*, 1908, [iv], **25**, 365; *A.*, 1908, ii, 455.

³⁰ B. Keetman, *Jahrb. Radioaktiv. Elektronik*, 1909, **6**, 265; *A.*, ii, 852; W. Markwald and B. Keetman, *Ber.*, 1908, **41**, 49; *A.*, 1908, ii, 144.

³¹ S. Meyer and E. von Schweidl-r, *Wiener Anzeiger. Sitzung.*, 11/6/09.

³² *Ann. Report*, 1907, 330.

³³ L. Haitinger und K. Ulrich, *Sitzungsber. K. Akad. Wiss. Wien*, 1908, **117**, (11a), 619; *Monatsh.*, 1908, **29**, 485; *A.*, 1908, ii, 857; H. Paweck, *Zeitsch. Elektrochem.*, 1908, **14**, 619; *A.*, 1908, ii, 917.

³⁴ J. Štěp, *Oesterr. Zeitsch. Berg. Hüttenwesen*, 1909, **57**, 155 and 173; *A.*, ii, 635.

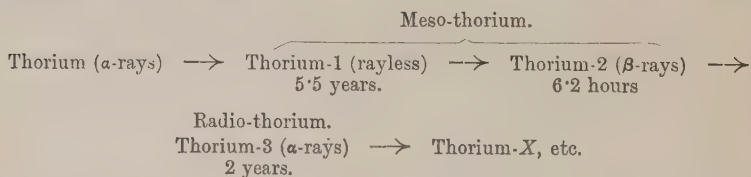
³⁵ B. Boltwood, *Amer. J. Sci.*, 1908, [iv], **25**, 493; *A.*, 1908, ii, 551.

is about 12 per cent. greater than the value deduced from the method of counting the number of α -particles expelled.

The spectroscopic data, from which the high value of 257.8 had been assigned to the atomic weight of radium, have been held to be capable of a different interpretation. The earlier value is based on a relation which is shown not to be exact for the case of the known atomic weights of the other elements in the alkaline-earth family. By means of a new interpolation formula which takes into account these differences, the experimentally found value 226.5 has been deduced from the same data.^{35A} Obviously the spectroscopic evidence is of little weight.

Thorium.

Further work on the β -rays of mesothorium³⁶ has shown that the latter substance consists of two successive products, for which the names thorium-1 and thorium-2 are suggested, the next product, radio-thorium, being, with this nomenclature, thorium-3. Starting from meso-thorium freed from radio-thorium by repeated purification, and precipitating in the solution a little added zirconium by means of ammonia, the precipitate contains thorium-2, possessing a β -radiation which decays exponentially to zero in some hours, whilst the filtrate yields a substance (thorium-1) giving at first no β -rays, but regenerating them exponentially with the same period as that at which the β -radiation of the first preparation decays. The period of half-change is given as 6.2 hours. The series now runs:



The half-period of radio-thorium (737 days) is obtained by direct observation,³⁷ and from it and the curves of the variation of activity of freshly-made thorium preparations with time, that of meso-thorium (thorium-1) is deduced to be 5.5 years.³⁸ Of the total α -activity of thorium in equilibrium with all its products, it has been deduced very neatly that 11 per cent. is due to thorium

^{35A} W. Marshall Watts, *Phil. Mag.*, 1909, [vi], 18, 411; *A.*, ii, 780.

³⁶ *Ann. Report*, 1907, 326; O. Hahn, *Physikal. Zeitsch.*, 1908, 9, 245 and 246; *A.*, 1908, ii, 454.

³⁷ *Ann. Report*, 1907, 324.

³⁸ H. N. McCoy and W. H. Ross, *J. Amer. Chem. Soc.*, 1907, 29, 1709; *A.*, 1908, ii, 81; O. Hahn, *Physikal. Zeitsch.*, 1908, 9, 392; *A.*, 1909, ii, 557.

itself, 20 per cent. to radio-thorium, and 69 per cent. to thorium-X and later products. The total α -activity of 1 gram is 1009 times that of 1 sq. cm. of the standard film of uranium oxide already described.

Atmospheric and Natural Radioactivity.

The amount of radium emanation in the atmosphere has been determined by condensation in charcoal at the ordinary temperature,³⁹ by condensation at liquid air temperature in metal tubes,⁴⁰ and in other ways.⁴¹ The amount varies widely in different localities and for the same place with atmospheric conditions, and is of the order of the equilibrium amount from 10^{-11} to 10^{-10} gram of radium per cubic metre of air. It is insufficient to cause more than a small part of the natural ionisation in the air, which is ascribed mainly to the penetrating radiation from radioactive elements in the earth's surface.⁴² The radium emanation has been detected in the atmosphere by means of its active deposit at great heights, up to 3000 metres, by the use of free balloons.⁴³

A number of investigations have shown that the thorium emanation plays a large part in producing the active deposit from the atmosphere, and that thorium is an agent in terrestrial radioactivity of importance comparable with uranium. In Rome⁴⁴ and Manchester⁴⁵ the equilibrium quantity of active deposit on a negatively charged wire after long exposure to the atmosphere was found to be mainly due to thorium. In New Haven (Connecticut) and California⁴⁶ the proportion is rather less, while at high places in the Alps little thorium could be detected.⁴⁷ The proportion probably depends somewhat on the potential to which the wire is charged. For Manchester it has been calculated that 1.4 times more thorium than uranium atoms break up per second in the earth's crust, so that there must be seven times more thorium present than uranium. Direct methods for the determination of thorium in common rocks have been worked out.⁴⁸ The Vesuvian

³⁹ J. Satterly, *Phil. Mag.*, 1908, [vi], 16, 584; *A.*, 1908, ii, 918; A. S. Eve, *ibid.*, 622; *A.*, 1908, ii, 919.

⁴⁰ G. C. Ashman, *Amer. J. Sci.*, 1908, [iv], 26, 119; *A.*, 1908, ii, 918.

⁴¹ W. Wilson, *Phil. Mag.*, 1909, [vi], 17, 216; *A.*, ii, 205.

⁴² K. Kurz, *Physikal. Zeitsch.*, 1909, 10, 834; Th. Wulf, *ibid.*, 997.

⁴³ S. Flemming, *ibid.*, 1908, 9, 801; *A.*, ii, 7.

⁴⁴ G. A. Blanc, *ibid.*, 295; *A.*, 1908, ii, 452.

⁴⁵ W. Wilson, *Phil. Mag.*, 1909, [vi], 17, 321; *A.*, ii, 202.

⁴⁶ H. Dadourian, *Le Radium*, 1908, 5, 102; *A.*, 1908, ii, 453; F. A. Harvey, *Physikal. Zeitsch.*, 1909, 10, 46; *A.*, ii, 203.

⁴⁷ A. Gockel and Th. Wulf, *ibid.*, 1908, 9, 907; *A.*, ii, 109.

⁴⁸ G. A. Blanc, *Le Radium*, 1909, 6, 306; *Phil. Mag.*, 1909, [vi], 18, 146; J. Joly, *ibid.*, 1909, [vi], 17, 760; 18, 140, *A.*, ii, 458, 637; R. J. Strutt, *Proc. Roy. Soc.*, 1909, 83, A, 97; *A.*, 1910, ii, 9.

lavas appear unusually rich both in thorium and radium. Fifty-one rocks from the St. Gothard Tunnel show on the average about two-thirds as much thorium as uranium (calculated from the radium). In the soil of Rome 1.45×10^{-5} gram of thorium per gram was found, and larger quantities in syenites and granites.

As an agent in the production of natural radioactivity, and in questions connected with the heat of the interior and underground temperature gradients, the importance of thorium appears co-equal with that of the uranium-radium series. On the important question as to the amount of radium in the ocean, considerable discrepancies exist in the results of different workers, and discussion may be deferred.⁴⁹ The amount is extremely small, although in the aggregate it must total a very large quantity.

Reference may be made to a work where the main geological bearings of radioactivity have been fully discussed,⁵⁰ which renders it the less necessary to deal with them in detail here.

Potassium.

A number of investigations have left no doubt as to the existence of a specific feeble β -activity from salts of potassium, which in all probability is a specific property of the element.⁵¹ Rubidium has also been shown to possess a distinctive β -activity far less penetrating than that of potassium.⁵² The value of $\lambda/d(\text{cm.})^{-1}$ of the potassium β -ray is given as 8, showing that it is only a little less penetrating than the radiation of uranium-X. For the rubidium radiation the value is 53. The activity of very thick layers of potassium salts is slightly greater than that of rubidium, but the specific activity of the latter, allowing for its greater absorption, must be seven times as great as the former. All attempts to concentrate the activity seem to have failed.^{52a}

Various.

Three other notable results may be briefly mentioned. The speed of crystallisation of superfused droplets of pure sulphur,

⁴⁹ J. Joly, *Phil. Mag.*, 1908, [vi], **15**, 385; **16**, 190; *A.*, 1908, ii, 246, 649; 1999, **18**, 396; *A.*, ii, 780; A. S. Eve, *ibid.*, 102; *A.*, ii, 633; W. Knoche, *Physikal. Zeitsch.*, 1909, **10**, 157; *A.*, ii, 287.

⁵⁰ J. Joly, *Radioactivity and Geology*. Constable and Co., 1909.

⁵¹ J. C. McLennan and W. T. Kennedy, *Phil. Mag.*, 1908, [vi], **16**, 377; *A.*, 1908, ii, 750; M. Levin and R. Ruer, *Physikal. Zeitsch.*, 1908, **9**, 248; *A.*, 1908, ii, 448; W. W. Strong, *Physical Rev.*, 1909, **29**, 170; compare *A.*, ii, 715; E. Henriot, *Compt. rend.*, 1909, **148**, 910; *A.*, ii, 458; E. Henriot and G. Vavon, *ibid.*, **149**, 30; *A.*, ii, 635; E. H. Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 154; *A.*, ii, 779.

⁵² N. Campbell, *Proc. Camb. Phil. Soc.*, 1909, **15**, 11; *A.*, ii, 288.

^{52a} Compare, however, E. Ebler, *Chem. Zeit.*, 1908, **32**, 812.

under the microscope, has been found to be increased by the β -rays of radium, whereas X -rays produced no effect. The effect is possibly to be associated with the charge carried by the β -rays.⁵³ The pleochroic halo in certain minerals has been associated with the α -rays of embedded granules of radioactive minerals producing changes in colour in the surrounding matrix. The radius of these halos corresponds closely with the range of the α -particle in the mineral.⁵⁴ In this way visual evidence has been obtained of quantities of radioactive matter only just within the range of the most sensitive electrical methods. A sensitive micro-balance on a new principle has been constructed capable of detecting changes in the weight (of an otherwise small constant load) if greater than 4×10^{-9} gram, which it is proposed to attempt to employ in following the weight changes in radioactive matter due to disintegration.⁵⁵ The balance, in the first place, is a gravity balance of the ordinary type, entirely constructed of fused quartz, the beam weighing less than 0.5 gram, carrying on one end as counterpoise a sealed quartz bulb containing a known amount of air. Balance is effected by varying the external pressure of the air in the balance case. Accordingly, as the external pressure is less or greater than that of the air in the bulb, the latter represents a small positive or negative weight of easily determinable amount. The pressure of the air in the balance case is adjusted until the beam remains at zero position.

FREDERICK SODDY.

⁵³ L. Frischauer, *Compt. rend.*, 1909, **148**, 1251; *Le Radium*, 1909, **6**, 161; *A.*, ii, 532.

⁵⁴ J. Joly, *Phil. Mag.*, 1907, [vi], **13**, 381; O. Mügge, *Centr. Min.*, 1907, 397; 1909, 65, 113, and 143; *A.*, ii, 286.

⁵⁵ B. D. Steele and K. Grant, *Proc. Roy. Soc.*, 1909, **82**, A, 580; *A.*, ii, 876.

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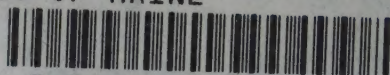
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